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DEPARTMENT OF COMMERCE

BULLETIN

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, Director

VOLUME 9

1913

WASHINGTON
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A NEW PRECISION COLORIMETER

By P. G. Nutting

It is well known that any color may be analyzed and specified in either of two different ways: (1) In terms of three primary components, red, green, and blue (*trichromatic* analysis); or (2) in terms of wave length of dominant hue or its complementary and per cent white (*monochromatic* analysis). In mathematical terms, the color point may be located by either trilinear or by polar coordinates. Of the three elements of color; hue, tone, and luminosity, *hue* and *tone* are determined with a colorimeter, *luminosity* with a photometer or a photometric part of the colorimeter.

Colors to be analyzed consist of light either *emitted* from some source, *transmitted* through some selective screen, or *reflected* from some mat or semi-mat surface. Any of these colors to be analyzed may be either *spectral* or *purple*, according to whether or not its dominant hue lies in the visible spectrum. Any analyzing colorimeter must then be applicable to emitted, transmitted, or reflected light of either spectral or purple dominant hue.

A trichromatic analyzer, the Ives[1] colorimeter, has been in successful use for several years. A monochromatic method of analysis was devised and used by Abney[2] in a laboratory investigation as early as 1890. The colorimeter here described is a monochromatic analyzer and was designed to be a practical working instrument of wide range, high precision, and of great simplicity.

---

[1] F. E. Ives: J. Franklin Inst., **164**, pp. 421–423; 1907.

[2] W. de W. Abney: Color Measurements and Mixtures, 1891, pp. 162–166.

The advantage of monochromatic analysis lies in the elimination of the arbitrary reference standards (red, green, and blue), readings being given directly in wave length and per cent white. Both methods involve the definition and adoption of some standard of white. The trichromatic method may be used for either spectral or purple hues indifferently; the use of the monochromatic method involves an interchange of two sources or arms in passing from spectral to purple hues. Both methods give readings varying somewhat with the observer, involving, in some cases, correction to the absolute color scale based on the average properties of a number of normal eyes.

The new colorimeter is so arranged that light of a pure spectral hue may be mixed with white light to match the unknown; or, in the case of purples, it is mixed with the unknown to match white. The match is made with a photometer cube.

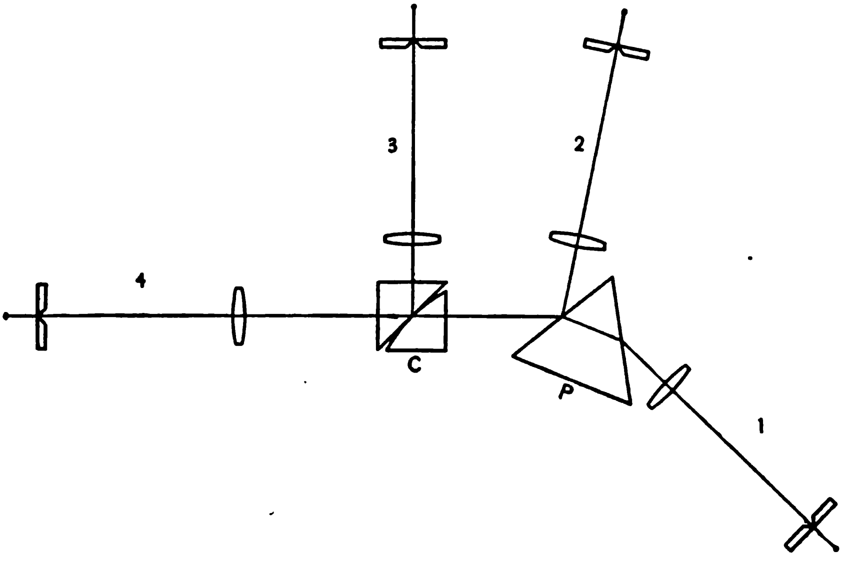

Fig. 1.—*Optical diagram of precision colorimeter*

Fig. 1 is a diagram of the optical parts of the instrument. Collimator 1 is movable; all the remaining parts are fixed. Collimators 1 and 4 with prism P form an ordinary spectroscope with pinhole ocular. The white and the unknown lights enter through collimators 2 and 3, in direct or in inverse order, according as the match is to be made with the dominant hue or its complementary. In analyzing reflected light the necessary collimator is raised or rotated or even removed entirely if sunlight is used.

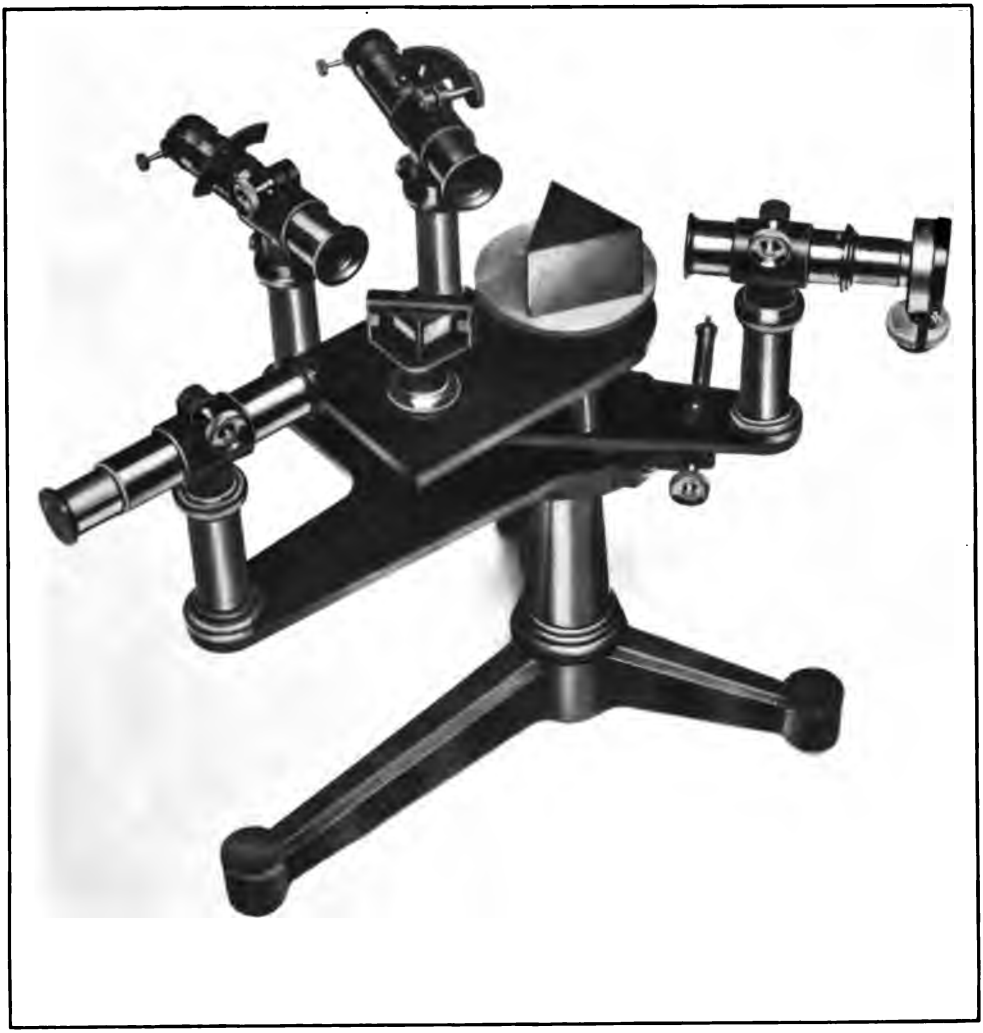

Fig. 2.—*Precision colorimeter*

Wave lengths are varied simply by rotation of collimator 1. Intensities may be varied by (1) varying slit widths, (2) rotating sectors, or (3) by rotating one of a pair of nicols placed just inside each slit. The colorimeter now in use is provided with a bilateral slit on the first collimator while collimators 2 and 3 are provided with pairs of nicols.

After a match has been secured, the wave length of the dominant hue is either read from the position of collimator 1 or is determined by throwing in a small hand spectroscope before the pinhole ocular of 4.

Intensities are determined by interposing between collimator 4 and photometer cube C, a white 180° (Whitman) rotating disk illuminated by a standard lamp. This gives the intensity in meter candles of each of the three component beams separately. Instead of this flicker photometer arrangement, a simple equality of brightness photometer may be used to determine the relative brightness of any two beams. To intercompare beams 1 and 2, for example, the top half of the objective of collimator 1 is covered with a black card and the lower half of 2 and then the width of slit 1 is varied until equality of brightness is secured. This slit width, compared with the original width used to secure a color match, gives the relative intensities of the two beams.

An experimental colorimeter of the type above described was assembled at the Bureau of Standards in the early spring of 1911 and given a thorough test. Later, special optical parts were ordered from Fuess and the instrument constructed in the Bureau shops. This new instrument has been in constant use at the Bureau since the first of January, 1912, in routine tests and special research work. A patent dedicated to the public has been granted.

Several sets of data are given below to show the sensibility of the instrument and the systematic errors to which its readings are subject. The first set was on a piece of the cover of this bulletin, a dull greenish gray, a fairly difficult test as regards wave length of dominant hue and per cent white but with reflecting power (luminosity) easily determinable. The second set was taken on a card colored a nearly spectral orange sent in as a secondary standard for test. On this the wave-length determination could be made with ease while the per cent white and reflecting power were difficult. The data is given as taken, no observations being rejected. Both observers have normal trichromatic vision. One observer (J) has a wave-length sensibility curve closely approximating that of the average eye, while the other observer (N) is abnormally sensitive to both quality and quantity of light in the yellow-orange region.

The sensibility is, of course, that of the observer's eye in each case, since the known and unknown fields are viewed side by side without a dividing line. The uncertainty in the wave length of the dominant hue is about 1 or 2 $\mu\mu$ except in the extreme red and and violet and for colors of very nearly a neutral gray or very dark shades.

TABLE I

Greenish Gray, Bulletin Cover

Dominant hue (in $\mu\mu$)		Per cent white		Reflecting power	
N	J	N	J	N	J
574	571	60	62	0.25	0.23
569	572	65	69	.27	.28
571	570	65	70	.26	.23
568	571	65	67	.28	.28
568	568	76	62	.27	.24
570	570	66	66	.26	.25

TABLE II

Mat Orange, Nearly Spectral

Dominant hue (in $\mu\mu$)		Per cent white		Reflecting power	
N	J	N	J	N	J
600	599	28	23	0.56	0.40
600	598	26	24	.59	.38
600	596	26	29	.53	.36
599	598	22	22	.66	.38
600	599	23	24	.55	.38
600	598	25	24	.58	.38

Complete color analyses of a few familiar and fairly definite colors are given in the following tables by way of illustration.

TABLE III

Source	Trichromatic analysis			Monochromatic analysis	
	Red	Green	Per cent blue	Dominant hue (in μμ)	Impurity (per cent white)
Blue sky	23.8	27.2	49.0	473	73
Cloudy sky	31.6	33.9	34.5		
Hefner flame	52.0	38.8	9.2	589	34
Carbon lamp (3.1 W)	48.3	40.4	11.3		
Acetylene	46.1	40.5	13.5	582	36
Tungsten (1.25 W)	44.9	41.1	14.0	587	37
Nernst (0.8 amp)	46.2	40.7	14.1	586	35
Moore tube (CO_2)	28.3	31.0	40.7		
Helium tube				591	33
Mercury tube				482	55
Neon tube				616	11

TABLE IV

Materials.	Monochromatic analysis		Reflecting coefficient
	Dominant hue (in μμ)	Impurity (per cent white)	
Sulphur	571	46	0.80
Cork	586	56	.26
Dandelion	580	9	
Tobacco leaf (medium)	597	65	.14
Chocolate	595	70	.05
Butter, light	580	45	
Butter, dark	580	28	.64
Navy blue (U. S.)	472	90	.019
Paris green	511	56	.386
Manila paper (about)	582	65	.57
Copper	597	70	.23
Brass, light	575	60	.32
Brass, dark	583	61	.28
Gold, medium	591	44	.21

The author is indebted to Mr. Lloyd Jones for making nearly all of the above determinations.

WASHINGTON, July 25, 1912.

INSTRUMENTS AND METHODS USED IN RADIOMETRY—II

By W. W. Coblentz

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I. INTRODUCTION

In the present paper an attempt is made to give the latest attainments in the construction of instruments used in measuring spectral radiation. In a future paper it is purposed to give an account of an intercomparison of various types of radiometers used in measuring undispersed ("total") radiation, including the determination of the same in absolute measure.

The arrangement of the subject matter follows closely the outline of a previous[1] paper on this subject, to which reference must be made for more complete information on certain topics.

The word "radiometer" will be used instead of the more clumsy expression "radiation meter," in speaking of these instruments in general, and to avoid confusion with the "Nichols radiometer" the latter will be distinguished by the use of the inventor's name.

To the familiar question "What instrument should I use?" the reply may be made that it is not always an easy matter to decide in the beginning of a new investigation which type of instrument will prove the most satisfactory. For work requiring the highest attainable precision with a great deal of routine observation, extending over a long period, the writer has adopted the vacuum bolometer because of its quickness of action and because of the wide range of variation and ease of testing its sensitivity. But the instrument is very elaborate and requires very careful handling. In many researches where the actual time consumed in observation is a matter of only a few weeks a radiomicrometer or thermopile would be sufficiently accurate, and would require less attention. The writer has both a vacuum bolometer and a thermopile in working order, and uses them with the same galvanometer.

II. THE RADIOMICROMETER

Within the past two years the radiomicrometer has come rapidly to the front as a competitor with the other types of radiometers, such as the Nichols radiometer, the thermopile, and the bolometer. The fact that it is not sensitive to magnetic disturbances makes this a very useful instrument deserving a more general adoption.

Féry[2] has recently described a radiomicrometer consisting of a loop of copper joined at the bottom by means of a short wire of constantan. The two junctions were placed at the same height, side by side, and covered with strips of silver 6 by 12 by 0.3 mm. The strips of silver were polished on the rear and blackened with platinum black on the front. For a candle and scale at 1 m the deflection was 23 cm.

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[1] This Bulletin 4, p. 391: 1908.

[2] Féry: Bull. Seances Soc. Franc. de Phys., p. 148; 1908.

One of the most noteworthy radiomicrometers described recently is the one constructed by Schmidt[3] in the laboratory of Prof. Rubens, and it has since been used by the latter and his collaborators in exploring the region of longest heat waves yet measured. The suspended system of Bi-Sb, as made by Schmidt, is practically the same as was previously described.[4] Instead of a glass rod at the top he used one of aluminum, 50 mm long and 0.5 mm diameter, and a mirror 4 mm diameter. The deflection on a 13 to 14 second period, without the concentrating funnel, was 20 cm, for a stearin candle at 1 m and a scale at 2.5 m, which is equivalent to 8-cm deflection for a candle and scale at 1 m.

Hollnagel[5] found that the instrument was subject to irregular deflections caused by air currents, the adiabatic expansions and compressions causing temperature variations in the thermojunctions. He therefore modified this instrument and placed it in a vacuum.

Using the conical receiver, Rubens and Hollnagel[5] observed a deflection of 10 cm for a candle at 6 m and scale at 3 m, for a single swing of 10 seconds. This is equivalent to 120 cm for a candle and scale at 1 m. Just how much the conical receiver has increased the apparent sensitiveness is unknown. In the original description of the Rubens thermopile,[6] the galvanometer deflection was given as 54 mm with the conical receiver and as only 22 mm without the receiver. A fair estimate of the radiomicrometer deflection, without the conical receiver, is therefore about 50 cm for a candle and scale at 1 m, the complete period being 20 seconds. The area of the exposed surface is not given, but judging from Schmidt's description of a linear junction of Bi-Cu, consisting of a strip of Bi, 18 by 1 by 0.4 mm, joined to a copper wire 0.13 mm diameter, and from the fact that the opening in front of the junction was 5 mm in diameter, the area of the receiving surface was of the order of 18 to 20 mm.^{2} However, since an ordinary candle gives readings 10 to 15 per cent higher than that of a standard sperm candle, and since the radiation tests were not made in the same manner as herein described, no accurate comparison can be made of these instruments. In the investigations of Rubens and Wood,[7] the sensitiveness of this instrument was increased so that, using the conical receiver, the deflection was increased to 70 cm (scale distance not given but probably 3 m as in previous work) for a candle at 2 m, the instrument being covered with a quartz window 1 mm thick.

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[3] Schmidt: Inaug. Diss. Berlin; 1909. Ann. d. Phys., **29**, p. 1003; 1909. Also used by Meyer, Ann. d. Phys., **30**, p. 612; 1909.

[4] This Bulletin, **4**, p. 391; 1908.

[5] Hollnagel: Inaug. Diss., Berlin; 1910. Rubens and Hollnagel: Sitzber. Akad. Wiss., **4**, p. 26; 1910, Berlin. Rubens and Wood: Sitzber., **52**, p. 1124; 1910.

[6] Rubens: Zs. f. Instk., **18**, p. 65; 1898.

In a previous paper,[8] the writer described a vacuum radiomicrometer. From later experience, it seems desirable to try constantan instead of bismuth as then used.

Recently [9] a new form of suspension was made for this radiomicrometer. The suspension consists of two junctions of bismuth and silver, with a copper loop, and it was made linear for spectral radiation work. It was found that by dropping the molten metal from a height [9] of about 1 m it would spatter out into a thin, well-annealed plate, which could then be rolled to 0.02 to 0.04 mm thickness. The dimensions of the present junction are: Bi= 8 by 1 by 0.03 mm, Ag=3 by 1 by 0.01 mm and copper wire=0.08 mm diameter. The central, active parts of the junctions were painted on one side with a mixture of platinum black, lampblack, and a little shellac in alcohol. The window covering the junctions consisted of a film of glass blown so thin that it showed interference colors. Such a film absorbs but little in the spectrum, except at 8 to 9μ.[10]

For a standard sperm candle at 3.1 m and scale at 1 m, with all extraneous light excluded except that which passed through a long, blackened tube, the deflection was 22 cm (for a single swing of 25 seconds) or more than 200 cm at 1 m. For a single swing of 10 seconds the deflection was at least 50 cm. It is therefore apparent that this form of junction is as sensitive as any heretofore described. The weight of the complete suspension was a little less than 10 mg. The sensitiveness of this suspension was not very much greater than that of a similar suspension having but a single thermojunction, which is in accordance with the theory

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[7] See footnote 5, p. 9.

[8] This Bulletin, **2**, p. 479; 1906.

[9] This Bulletin, **7**, p. 243, 1911. Since writing this paper Pfund (Amer. Phys. Soc., meeting Dec. 27, 1911) has described a similar method, which enabled him to produce fine filaments of the order of 0.01 mm diameter. (See Phys. Rev., **34** p. 228; 1912.)

[10] See Investigations of Infra-Red Spectra, Vol. II, p. 65; 1906.

The purpose in describing this form of instrument is not so much to show its sensitiveness as to indicate directions in which further improvements are possible. On account of the difficulties in preparing a nonmagnetic loop, there is still much room for improvement by combining the Nichols radiometer and the radiomicrometer. For detecting electrical waves the system can be made still lighter and the heating arrangement can be brought close to the junction as in the Duddell[11] ammeter, or by using a Klemenčič thermojunction[12] and radiomicrometer as described by Pierce.[12] The point receiver thermopiles of bismuth and silver, described on a subsequent page, would be more sensitive and quicker acting than obtains in the present commercial instruments (e. g., ammeters).

In table I are shown the radiation sensitivities of various radiomicrometers for which comparative data are available.

TABLE I

Sensitiveness of Radiomicrometers and Rubens Thermopile

Observer	Full period	Area of vane	Deflections in cm/mm², candle and scale at 1 m
	sec	mm²	cm
Boys	10	4	0.9
Phil. Trans., 180 A, p. 159, 1889.			
Paschen	40	....	3.0
Wied. Ann., 48, p. 275, 1893.			
Lewis	20	1.4	1.3
Astrophys. Jour., 2, p. 1, 1895.			
Coblentz	40	3	3.6 (in air) Bi-Sb
	25	3	6.0 (in vacuo)
This Bulletin, 2, p. 479; 1906.	16	5	5.0 (in vacuo) Bi-Cu
Ibid. 7, p. 248; 1911	50	10 to 12	20.0 in air

With the electrically heated welding device described on a subsequent page (Fig. 1) a much greater refinement in construction and a higher sensitivity should be attainable. With this end in view, very much smaller and lighter (3 to 5 mg) suspensions should be tried in place of those heretofore employed.

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[11] Duddell: Phil. Mag. (8), 2, p. 91; 1904; Jour. de Phys. (4), 4, p. 5; 1905.

[12] Pierce: Amer. Jour. Sci., 9, p. 252; 1900. Klemenčič, Ann. der Phys. (3), 45, p. 62; 1891.

III. THE THERMOPILE

1. BRIEF DESCRIPTION OF THERMOPILES OF RECENT CONSTRUCTION

During the past year or two, numerous attempts have been made to further improve the linear thermopile, principally by the use of finer wires as already indicated.[13] Soon after writing the paper cited above, an investigation was published by Moll[14] in which he used a modified form of Rubens thermopile of 30 elements. The iron-constantan wires were 0.06 mm diameter, the junctions were about 0.2 mm^2 area, the area of the exposed surface being about 0.42 by 11 mm and the resistance about 12 ohms. The galvanometer sensitivity was 1.1×10^{-10} ampere with a complete period of 12 seconds. The weak point in the design of Moll's thermopile arose from joining the "cold" (unexposed) junctions to the heavy metal support instead of having them free as in the original design of Rubens. The hot and the cold junctions, therefore, always had a different temperature (owing to a difference in heat capacity and in emissivity) which caused a large permanent deflection, and a drift in the zero reading. However, by surrounding the instrument with a water-cooled envelope he was able to do excellent work with it.

In passing, attention should be called to a thermopile in the form of an annulus, known as a "coronal thermopile," used by Callendar[15] on a solar eclipse; also to a theoretical paper by Altenkirch[16] on the efficiency of thermocouples, in which he shows that the external resistance can be two to three times the internal resistance of the pile, without seriously affecting the maximum efficiency of the pile.

Paschen[17] constructed a thermopile of iron 0.1 mm and of constantan 0.08 mm in diameter. The constantan wire was 4 mm long. The wires were mounted end to end and fused with a little borax and silver solder. The junctions and wires were then rolled to 0.002 mm thickness. The number of junctions and the resistance was not given. The maximum temperature was attained in four seconds and 98 per cent of the inrease in two seconds. The sensitivity was about the same as that of a bolometer strip 0.001 mm thickness but was only about one-half that of his best bolometers on high battery current; its manipulation, however, was easier.

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[13] This Bulletin, **4**, p. 391; 1908.

[14] Moll: Inaug. Dissertation Utrecht; 1907. Archives Néerlandaises des Sci., Serie II, Tome XIII, p. 100.

[15] Callendar: Proc. Roy. Soc., **77 A**, p. 8; 1905.

[16] Altenkirch: Phys. Zs., **10**, p. 560; 1909.

[17] Paschen: Ann. der Phys., **33**, p. 736; 1910.

Reinkober[18] constructed a vacuum thermopile of 14 junctions of iron-constantan, of wires 0.05 mm diameter and having a resistance of 14 ohms. It was 3 times as sensitive as the old form of Rubens pile with wires 0.15 mm in diameter. In vacuo it was 1.6 times as sensitive as in air. He made also a thermopile (of wires 0.021 mm thickness, hammered thin) of only four elements, since the resistance was 18 ohms. In air, this was twice as sensitive as the old form, and in vacuo 10 times as sensitive as the commercial Rubens instrument. He found that its sensitivity was only one-half that of a vacuum bolometer.

Johansen[19] has made a study of vacuum thermopiles of iron-constantan and of iron-bismuth. From theory he finds that (1) the resistance of the thermopile should equal that of the galvanometer, (2) the radii of the two wires of the element should be so chosen that the ratio between the heat conductivity and the electrical resistance is the same in both, (3) the heat loss by conduction through the wires should equal the heat loss by radiation from the junctions, (4) the radiation sensitivity is proportional to the square root of the exposed surface. In an iron-constantan couple the theory required the use of iron wire 0.023 mm and constantan wire 0.045 mm diameter; and for a Bi-Fe couple iron wire 0.024 mm and bismuth wire 0.075 mm diameter. If the diameter of both wires were twice as great, theory indicates that the sensitivity would be only 0.8 the maximum sensitivity. He used a single long junction consisting of a constantan wire 0.03 mm and an iron wire 0.015 mm diameter soldered to a strip of silver 10 by 0.2 by 0.015 mm. By allowing the radiation to fall on different parts of this long junction he found that the radiation sensitivity varied only a few per cent over the whole length. For a junction 0.5 cm long, this variation was 0.9 per cent, which is entirely different from a bolometer strip which has its maximum radiation sensitivity at the middle and zero sensitivity at the ends. He claims that the "temperature sensitivity" of the Rubens pile is 10 to 15 times greater, but that the "radiation sensitivity" is much less than for his instrument. Calling the radiation sensitivity of the Reubens pile 1, then that of his vacuum pile of iron-constantan is 4.5, of Bi-Fe is 9.5 and of his vacuum bolometer is 9.7. The iron-constantan pile required an exposure of 20 seconds and the Fe-Bi pile required 30 seconds to attain a temperature equilibrium.

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[18] Reinkober: Ann. der Phys., (4), **34**, p. 349; 1911.

[19] Johansen: Ann. d. Phys. (4), **33**, p. 517; 1910.

Spence[20] has recently constructed a sensitive thermopile of two elements (1) an alloy of Bi + 5 per cent Sn and (2) Bi + 3 per cent Sb. The thermoelectric power was 120 microvolts (iron-constantan = 53). These alloys were pressed into sheets about 0.25 mm in thickness and then cut into bars 2.5 by 0.5 mm. A pile of 37 elements presented an exposed surface of 21 by 0.5 mm. It had a resistance of 5 ohms and a thermal e m f of 4.4 milli-volts per degree. Using a galvanometer having a sensitivity of 4×10^{-10} amperes, a deflection of 1.4 mm (against Rubens = 0.4 mm) would occur for 1×10^{-6} degree rise in temperature. Under this condition a candle at 1 m gave a deflection of 234 cm. He says that a good bolometer would give a deflection of 250 cm under similar conditions. He found the pile sluggish, and it had a slow drift which resulted, no doubt, from the lack of thermal equilibrium of the hot and the cold junctions. This is to be expected, for its heat capacity is almost as great as that of the old type of thermopiles. Moreover, because of this defect, the large temperature sensitivity (120 microvolts per degree per couple) is not a true indication of its radiation sensitivity. The original Rubens pile of 20 junctions of iron-constantan gave a deflection of 250 cm when using a galvanometer about twice as sensitive as the one used by Spence. It therefore appears that, using the same number of junctions, the Spence type of thermopile has no particular advantage over the one of iron-constantan when a comparison is made of the radiation sensitivity of the two instruments.

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[20] Spence: Phys. Rev., **31**, p. 666, 1910. (See also a paper by Hutchins, Amer. J. Sci., **48**, p. 226, for the alloys used.)

The main defect in a thermopile of fine iron wires is the rapidity with which which they rust. They should therefore be given a thin coat of shellac. Since the thermoelectric power of copper-constantan is not markedly different from that of iron-constantan (Fe-Const. = 51 to 53 mv; Cu − Const. = 40 to 41 mv) it seems advisable to use copper instead of iron.

2. CONSTRUCTION OF A BISMUTH-SILVER THERMOPILE

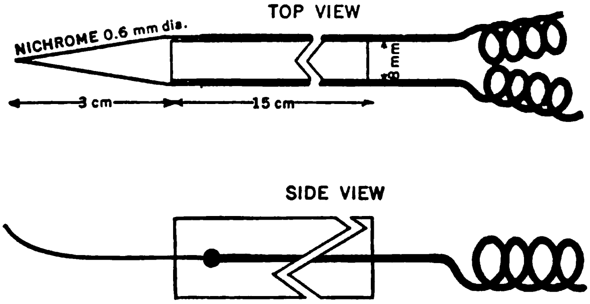
The main defect in a thermopile is its great heat capacity with the consequent lag in attaining temperature equilibrium. This is apparent in nearly all of the designs just described. Furthermore, the more sensitive thermopiles can not be made into commercial instruments.

In the instruments now to be described, the success attained in construction results from the use of the electrically heated welding device and from the choice of wire (silver) which is easily freed from sulphide. The silver wire contributes but little thermoelectrically, but this is compensated by its extremely low resistance, which is about 0.07 ohms per centimeter for wire 0.05 mm in diameter. One need not, therefore, exercise any great care in making the silver wires of a minimum length to produce a low resistance thermopile. A preliminary heating brightens and anneals the wire; a procedure which can not be followed in cleaning copper and iron wire. The use of pure tin in welding produces an alloy which is not brittle. The construction of the thermoelements of bismuth and silver is therefore an easy process, so that after attaining some skill they can be made at the rate of 15 to 20 per hour. The instrument can, therefore, be built in any laboratory, and of the proper design to suit the problem under investigation.

(*a*) **Linear Thermopiles.**—An attempt was made to construct a thermopile of bismuth and iron using fine bismuth wire (from Hartmann and Braun) and fine iron wire, and soldering with Wood's alloy. The further addition of bismuth, resulting from melting of the bismuth wire made a very brittle junction. To make good contact the iron wire was given a coating of pure tin, but that did not appear to remedy the matter. It was very difficult to thoroughly clean the iron wire; and the further difficulty of annealing it made the construction of the thermoelement very laborious. It was found that the resistance of a single junction rose from 1.5 ohms to 3 ohms and sometimes to 90 000 ohms in a few days, so that this type of thermojunction was discarded.

There is no particular advantage in using iron instead of silver, in view of the fact that iron rusts easily; that the Bi-Fe junctions are weak; and that although the thermoelectric power of iron is about 5 times that of silver, its resistance is from 6 to 10 times that of silver.

The welding of bismuth to silver makes a very strong junction. It was found that the direct welding of bismuth to silver was difficult. A small bead of pure tin, about 0.1 mm in diameter was therefore melted to the silver wire (Ag = 0.051 mm diameter) by means of a small heater of nichrome wire (nickel or iron wire would probably be just as serviceable) filed thin at the point, shown in Fig. 1. The end of the bismuth wire (0.1 mm diameter) was then brought in contact with this bead of tin (probably an alloy of Sn and Ag) which is then melted with the nichrome heater. Such a heater is better adapted to delicate work of this type than is a well-tinned soldering copper, the surface tension of the molten material on the hotter surface of an ordinary soldering instrument being sufficient to tear fine bolometer strips. The



NICHROME SOLDERING INSTRUMENT
Fig. 1

bismuth wire is too brittle to permit flattening the junction, so that a small rectangle of pure tin 1.4 by 0.6 by 0.025 mm was then placed under the Bi-Ag junction and fused thereto with a light touch of the nichrome heater. It is somewhat easier to flatten the tin bead attached to the silver and then fuse the bismuth to this flat disk, as shown in the lower part of Fig. 2, but in this case it is not so easy to produce a receiving surface which completely fills the thermopile slit.

There are many points in favor of the use of silver instead of copper wire in this type of thermopile. It is easily annealed and the tarnish is easily removed by heating the wire on a sheet of metal. Thus cleaned the bead of tin is attached without any soldering acid. A bit of rosin is useful but not necessary in attaching the bismuth wire. The low resistance, and especially the pliability of the silver are also important advantages, which one appreciates after working with (unannealed) iron and constantan wires. The bismuth wire is not so pliable but it is short and, since it is subject to but little handling in mounting, is not liable to be broken.

Before mounting, each junction was given a thin coat of shellac on the rear side for insulation, and the front surface was painted with a mixture of equal parts of lampblack and chemically precipitated platinum black in a dilute alcoholic solution of shellac. The amount of shellac to be added is just sufficient to cause the material to adhere well to the metal surface. This produces a hard, compact, matte surface which permits the removal of dust. The platinum black increases the thermal conductivity. Using receivers of equal size, it was found that the radiation sensitivity of the receiver covered with the mixture of lampblack and platinum black was 1.5 as great as the one painted with pure lampblack. This is a question which requires further investigation.

The junctions were then mounted upon a glass plate with Le Page's glue, the edges slightly overlapping, as shown in the upper part of Fig. 2, and the ends of the silver wires were soldered together. The glass plate was then mounted on an ivory frame and the loose ends of the silver wires were attached to the latter with shellac after which the glass plate was removed by soaking in water, thus leaving a uniform, solid, well-insulated receiver, as shown in Fig. 3. Subsequently, all these junctions were separated and the resistance of the pile was then found the same as when the junctions were in contact, showing that the insulation was perfect. The silver wires were then given a thin coating of shellac, but this is not necessary. The length of the receiving surface of this pile of 20 junctions is 12 mm. The great width, 1.3 to 1.4 mm, of this particular pile was chosen for a special research which required high sensitivity. The rectangles or disks of tin could be made much smaller as in the new form of Rubens thermopile.

The thermal emf of this bismuth-silver thermocouple is 89 microvolts per degree as compared with 51 to 53 microvolts for an iron-constantan couple. The temperature sensitivity of Bi-Ag is therefore about 71 per cent greater than that of an iron-constantan thermopile. Whether the radiation sensitivity is increased in like proportion depends upon the selection of the proper diameters of wires. As shown later, the radiation sensitivity of this thermopile is 2.5 to 3 times that of the iron-constantan pile. The new form [21] of iron-constantan thermopile of fine wires has a resistance of about 9 ohms. The above thermopile of bismuth-silver has a resistance of 9.3 ohms. By using bismuth 0.6 mm diameter the resistance would be much higher.

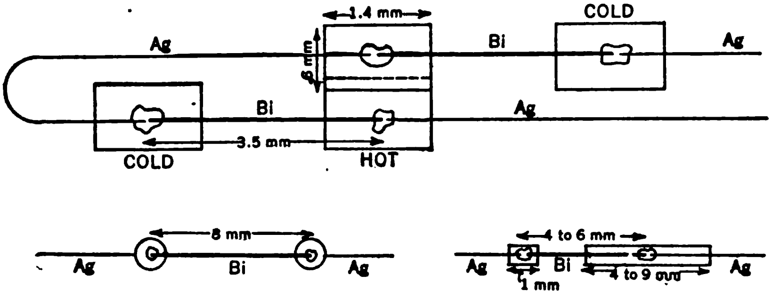


Fig. 2

The radiation sensitivity of this bismuth-silver pile and of an iron-constantan pile were compared, by means of a galvanometer of 5.3-ohms resistance and a sensitivity of 4.6×10^{-10} ampere.

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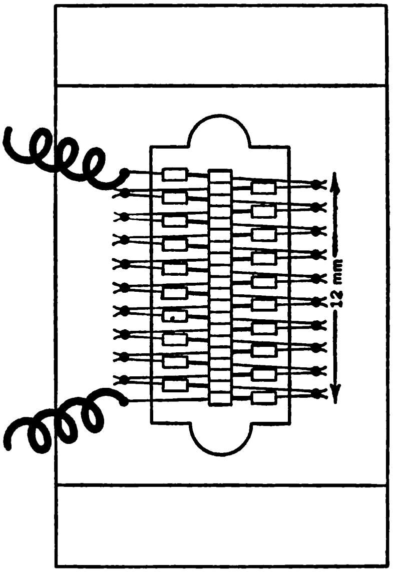
[21] This Bulletin, 4, p. 391; 1908.

Using first the bismuth-silver pile, a standard sperm candle placed at a distance of 2.4 m caused a deflection of 10.2 cm (or 59 to 60 cm for a candle and scale at 1 m). With a galvanometer sensitivity 3 times as large as ordinarily used, the total deflection (in air) would have been about 180 cm. This is only about one-half as sensitive as the vacuum bolometer to be described presently, but in vacuo it would be as sensitive as the vacuum bolometer.

The Rubens iron-constantan thermopile, with wires about 0.15 mm in diameter and having a resistance of 4.7 ohms similarly exposed, caused a deflection of 3.8 to 4.0 cm (or about 23 cm for a candle and scale at 1 m). The receiving surfaces of this pile were about 1.5 mm diameter and about 0.2 mm thick. The disks overlapped so that the 20 junctions occupied a space 20 mm long. The actual area exposed was therefore greater than in the Bi-Ag pile, which had a receiving surface of about 16 mm^2. This comparison shows that the radiation sensitivity of the bismuth-silver is about 2.6 times that of the ordinary Rubens thermopile. If we consider that in spectroradiometry we are interested in the length of the spectral line which can be utilized, we should have made the length of the Bi-Ag pile 20 mm, by adding more couples. The radiation sensitivity of the Bi-Ag pile would therefore be increased in the ratio of 20 to 12, which would give a total deflection of about 100 cm instead of 60 cm as observed. It is therefore safe to say that, comparing equal lengths of receiving surface utilized on a spectral line, the radiation sensitivity of this type of bismuth-silver pile is 4 times that of the old type of low resistance, iron-constantan pile. If we compare the bismuth-silver with the



Bi-Ag THERMOPILE

Fig. 3

fine wire type[22] of iron-constantan pile, which has a resistance of 8.9 to 9.3 ohms and a radiation sensitivity 1.4 times that of the old type of Rubens pile, it is a fair estimate to say that this bismuth-silver pile has a radiation sensitivity at least 3 times as great as the new type of iron-constantan thermopile.

One important point usually not considered is the heat capacity and hence the speed of attaining temperature equilibrium in these instruments. In the present radiation sensitivity tests the half period of the galvanometer was 2 seconds. When joined with the bismuth-silver pile the half period was lengthened to about 3.8 seconds, which is practically the same as with the new type of fine-wire iron-constantan pile described in a previous paper.[22] This is not an excessively long period and the galvanometer mirror returns quickly to its zero position. With the old heavy-wire type of iron-constantan pile, the time of single swing of the galvanometer was increased from 2 seconds to about 6.5 seconds and there was a tendency to lag, especially when measuring intense radiation, so that it does not compare favorably with the bismuth-silver pile.

This thermopile of bismuth-silver was designed for special work requiring a large receiving surface in air where very thin metal is easily affected by air currents. The hot and the cold junctions are sufficiently alike in size and emissivity so that no temperature difference and consequent drift is produced in the galvanometer deflection. The junctions are easily made and mounted, and are equally easy to repair if broken. The iron-constantan pile of fine wire is difficult to handle and difficult to repair if broken.

By using an alloy of platinum-iridium instead of silver the thermoelectric power would be increased, but owing to the increased resistance it remains to be determined whether a higher radiation sensitivity would be obtained.

The present instrument is not intended for rapid work, but to give exact and undisturbed readings with the instrument in air. The time to attain temperature equilibrium is about 4 seconds, but by reducing the heat capacity (using finer bismuth wire) temperature equilibrium should be attained in less than 3 seconds. In another comparison test, using a more intense radiation (acetylene flame), the bismuth-silver pile attained temperature equilibrium in 6 to 7 seconds, while the Rubens pile required from 25 to 30 seconds. The two piles being similarly mounted, one can assume that this is owing to the great difference in the heat capacity of the two kinds of thermojunctions.

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[22] This Bulletin, 4, p. 391: 1908.

The logical procedure in this investigation would have been to test various combinations of bismuth and silver wires before constructing a thermopile; but the marked success attained was not anticipated, and the following experiments were made on silver wire procured afterwards.

In the experiments on surface thermopiles, to be described presently, it was found that bismuth wire 0.15 mm diameter has a too great heat capacity, so that half a minute was required to attain thermal equilibrium, and that bismuth wire 0.1 mm diameter was very satisfactory. The question, therefore, to be solved was the size of the silver wire to be used with 0.1 mm bismuth wire in order to attain the maximum radiation sensitivity. The dimensions of the tin receivers were 2.5 by 0.03 mm. All the comparisons were made against a standard junction, A, with silver wire 0.0513 mm in diameter; the other junction, B, being made with silver wire of small diameter, say, 0.04 mm. The intervening bismuth wire was about 4 mm long. These elements were mounted over an opening in thick cardboard and covered with glass plates to avoid air currents. The source of radiation was an acetylene flame, and the comparison was made by exposing alternately the standard junction, A, of 0.05 mm silver wire and the one under investigation, B.

Using an element with silver wire, $B = 0.0410$ mm diameter, the ratio of sensitivities $B \div A$ was 1.13. In other words, a thermopile, in which the bismuth wire is 0.1 mm diameter and in which the silver wires are 0.04 mm diameter, would have a radiation sensitivity which is about 13 per cent higher than the one just described of silver wires 0.05 mm diameter. The latter contains about 20 cm of silver wire having a resistance of about 1.4 ohms, the total resistance of the pile being about 10 ohms. The total resistance of a pile of 20 junctions having silver wire 0.04 mm diameter and bismuth 0.1 mm diameter would therefore be from 11 to 12 ohms.

Using an element with silver wire, $B = 0.030$ mm, the ratio of sensitivities $B \div A$ was 1.20. The two receivers were then reblackened and the ratio was 1.195. In a vacuum the sensitivity was doubled by reducing the pressure to about 0.15 mm. With a lower pressure the sensitivity would of course be still further increased. A pile of 20 elements having silver 0.03 mm in diameter would have a radiation sensitivity about 20 per cent higher than the one herein described, and its resistance would be from 13 to 14 ohms.

Using silver wire 0.021 mm diameter, the ratio of B ÷ A was 1.12. The same value was obtained on repainting the receivers. The resistance of such a pile of 20 elements would be from 18 to 19 ohms. Its radiation sensitivity in air would be about the same as that of a pile having silver wires 0.04 mm diameter, and hence there is no advantage in using the finer wire. The loss by convection is usually found to be greater from fine wire so that, in a high vacuum, the radiation sensitivity might be considerably increased when using a small receiver and fine silver wires. In the present tests the sensitivity was increased 70 per cent in a vacuum of about 0.15 mm pressure. This increase in sensitivity is somewhat less than found in the element having 0.03 mm silver wire. These tests show that the size of the wire is not an important factor at this gas pressure.

From the aforesaid experiments it appears that the most sensitive thermopile of bismuth wire 0.1 mm diameter is obtained by using silver wire 0.03 mm in diameter. It appears advisable, however, to apply a coat of lacquer to wires of this fineness to avoid a change in resistance, which may result from tarnishing of the wire.

(*b*) **Surface Thermopiles.**—The success attained with the linear pile led to the construction of a thermopile having a large receiving surface, built up of single units, each of which contains 20 or more thermoelements mounted upon an ivory support as shown in Fig. 4, C. In the preliminary tests to determine the most desirable width of strip to be used, thermoelements were built with receivers of the same width, 0.6 mm, and of different lengths, as shown in the lower part of Fig. 2. In all cases the silver wire used was 0.0513 mm diameter. The bismuth wires (4 to 5 mm long) were 0.06 and 0.15 mm in diameter. The two receiving surfaces (1 by 4 mm, or 1 by 9 mm) were blackened, and exposed alternately to radiation. The elements to be tested were inclosed in order to avoid air currents.

Using bismuth wire 0.15 mm in diameter, the deflection for a receiver 4 mm long was not quite twice that of a receiver 1 mm long. For both receivers the deflection did not attain a maximum abruptly; and there was a serious creeping, requiring some 15 seconds for the galvanometer to come to rest.

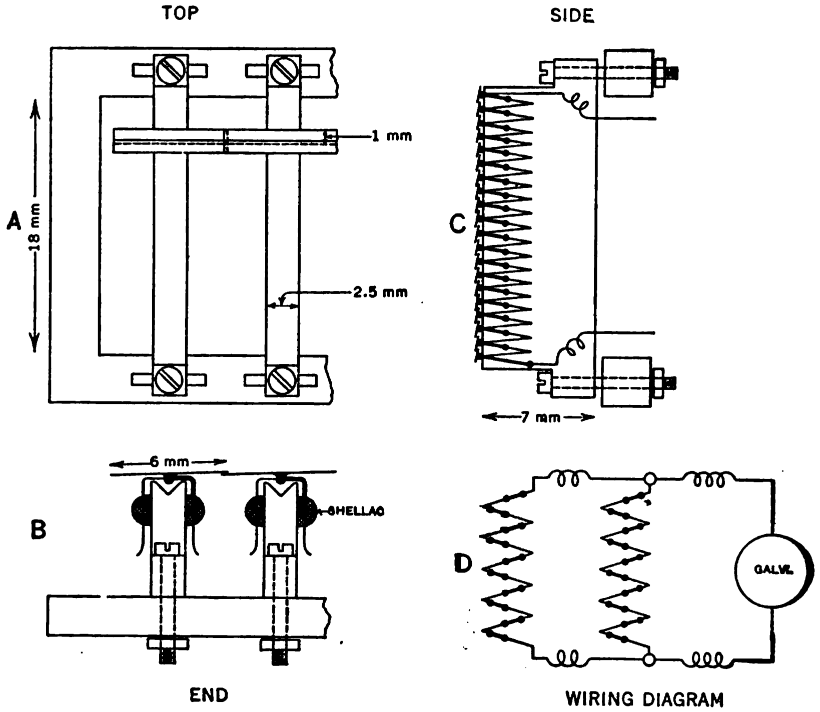

Fig. 4

Using bismuth wire 0.06 mm in diameter, the galvanometer deflection for a receiver 4 mm long was 2.1 times as large as that for a receiver 1 mm long. On reducing the length of the 4 mm receiver to about 2.6 mm, the sensitivity was 1.9 times as great as for the receiver 1 mm in length. A receiver 9 mm long was 2.7 times as sensitive as a receiver 1 mm in length. As shown in Fig. 5, the sensitivity varies roughly as the square root of the receiving surface, which is the law of the surface bolometer. As a matter of fact, there is an optimum length, which is of the order of 2 mm, but the exact value was not determined. Obviously, two receiving surfaces 4 mm wide are better than a single one 9 mm wide in the ratio 4.2 to 2.7. In fact, the sensitivity should be still greater than this (if a galvanometer having a resistance of the same magnitude be provided), for by placing the two units (4 mm wide) in parallel, the internal resistance is reduced to one-half the former value. Units which are built up with receiving surfaces 4 to 6 mm wide give ample working space in mounting, so that there is a distinct gain in using such narrow widths.

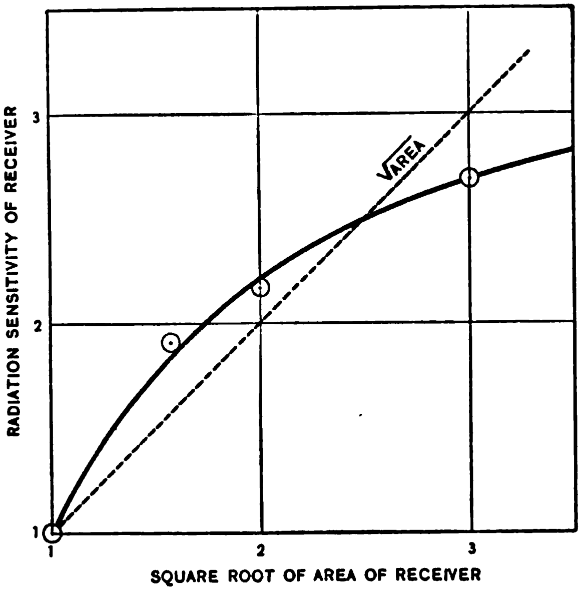

Fig. 5

No difference could be detected in the sensitivity of the front and the rear surfaces of these junctions, showing that attaching the junction at the center of the receiver is not detrimental.

The size of the receiver made no appreciable difference in the time of attaining a temperature equilibrium. In constructing a surface thermopile for experimental tests it was therefore deemed permissible to omit the receiving surfaces from the unexposed junctions. The results show that unless the instrument is well shielded, there may be drift as found by Moll. With the fine bismuth wire the deflection attained its maximum abruptly in 3 to 4 seconds.

In a vacuum of 0.15 mm pressure, the thermoelement of bismuth wire, 0.06 mm in diameter, was 2.03 times as sensitive as in air. The sensitivity would be further increased in a higher vacuum. It is, therefore, a distinct advantage to place the pile in an evacuated inclosure.

Using receivers of the same size, the radiation sensitivity of a thermoelement of bismuth wire 0.15 mm (and silver wire 0.05 mm) in diameter was twice as great as that of an element of bismuth wire 0.06 mm in diameter, as indicated by theory.[23] But the serious lag in attaining temperature equilibrium in a thermopile of bismuth wire 0.15 mm in diameter is objectionable, so that it is to be recommended only where a very high sensitivity is required and where the radiation to be measured is very weak.

In the surface thermopile it was therefore decided to use bismuth wire 0.1 mm and silver wire 0.05 mm in diameter, which increases the radiation sensitivity to nearly that of an element with bismuth wire 0.15 mm in diameter, while the time of attaining temperature equilibrium is about the same as that of the element having bismuth wires 0.06 mm in diameter. If the various elements are joined in parallel, as shown in Fig. 4, D, the resistance is reduced and the sensitivity is increased. By having the units uniformly exposed to radiation, so that each unit produces the same voltage, there will be but little shunting of the current generated. It is therefore important to have the units of the same heat capacity and emissivity, equality of resistances being of minor importance.

In making the units, the insulated, blackened, individual elements are mounted in a row, upon a glass plate, as previously described for the linear pile, and the silver end wires are soldered together. The ivory support is then placed over the central line of receivers, and the end wires are bent back against the side of this support (shown in Fig. 4, B, C) and attached thereto, along the side, with shellac. No shellac is permitted to come in contact with the "hot" junction, which would affect the heat capacity.

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[23] Johansen: Ann. d. Phys., (4) **32**, p. 517; 1910.

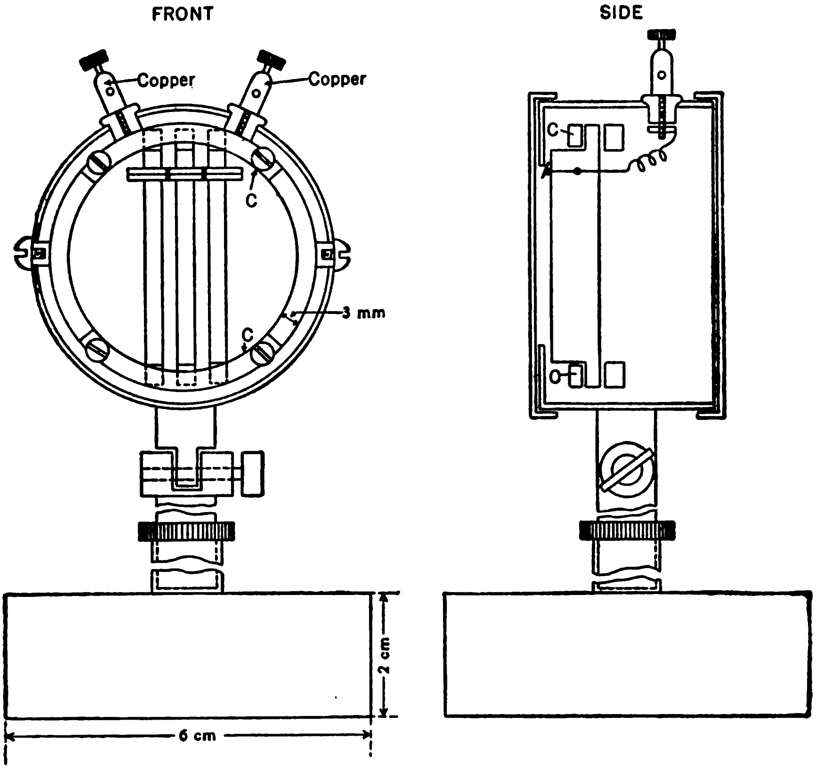
The sensitivity and heat capacity are not affected by having this junction in contact with the ivory support. In the latest design, however, the active junction is suspended across a slot in the ivory support. The mounting of the elements is the most delicate part of the work, as the bismuth wires become brittle after bending them several times. Since the wires are bent away from the receiving surface, before mounting (Fig. 4, B), in order to apply the insulating coat of shellac on the rear surface, it is best to leave them thus throughout the remainder of the construction. A small bead of solder is attached to the end of each one of the silver wires before mounting the elements on the glass plate, and it is then an easy matter to connect them with the nichrome heater. It is necessary, however, to hold the wires with tweezers to prevent heat from being conducted to the bismuth, which would melt the junction.

After the shellac has dried, and the pile has been separated from the glass plate by soaking in water, the elements are very securely held to the ivory mounting and there is little danger of breaking them. Because of the fragility of the bismuth wire, in mounting it might be better to use a different form of holder than the one here described, and join the bismuth-silver junction to the tin receiver as shown in Fig. 7, C.

The mounting for these ivory supports (Fig. 4, A) may be of brass, and, for convenience in construction, may be circular, as shown in Fig. 6. The slight adjustment of the ivory supports, necessary in placing them upon this mounting, is accomplished by means of slots and bolts, as shown in Fig. 4, A, or by means of clamps, *e*, as shown in Fig. 6. In Fig. 6 is shown a surface pile made of three units each consisting of 20 elements. The individual receivers are of tin 6 by 1 by 0.03 mm, and the total area is about 17 by 17 mm. The instrument was designed for psychological work, in which it is desired to measure a light stimulus 15 mm in diameter.

The three individual units have closely the same resistance and the same radiation sensitivity; but in overlapping them to form a continuous surface there is no doubt a slight loss in sensitivity. With the short period galvanometer used, it could not be determined whether there was a difference in the time required for each of the three units (joined in parallel or series) to come to thermal equilibrium. This would cause the galvanometer deflection to approach a maximum at an irregular rate.

Using the three units in series (resistance 33.6 ohms), and a galvanometer resistance of 5.3 ohms and $i = 6.5 \times 10^{-10}$ ampere, a standard sperm candle at a distance of 3 m gave a deflection equivalent to 166 cm at 1 m. For a galvanometer sensitivity of $i = 2 \times 10^{-10}$ ampere, as ordinarily used, this would be about 560 cm deflection for a candle and scale at 1 m. This is about 4.2 times the deflection of the aforesaid linear pile used under similar conditions. It attained thermal equilibrium in the same time



HOLDER FOR THERMOPILE

Fig. 6

(in 2.5 to 3 seconds, for a galvanometer half period of 1 second) as obtained with the linear thermopile.

With the three units joined in parallel (resistance 3.8 ohms) and with a galvanometer sensitivity of 6.8×10^{-10} ampere, the deflection for a candle at 2 m was equivalent to 227 to 230 cm at 1 m. For a sensitivity of 2×10^{-10} ampere this would correspond to 770 to 780 cm for a candle and scale at 1 m. This is about 6 times (the values, obtained on different days, varied from 5.9 to 6.05) the sensitivity of the linear pile. The galvanometer half period was increased from about 1 second to 3 seconds when the pile was exposed to radiation.

From a consideration of the areas of the individual receivers, the surface thermopile should have been 7.3 to 7.5 times as sensitive as the linear pile. In view of the fact that this is the first instrument of the present type of surface thermopile ever constructed, the agreement between theory and experiment (experiment $= \frac{6}{7}$ theory) is fairly satisfactory.

As shown on a previous page, by using finer silver wire (silver 0.03 mm, bismuth 0.1 mm) the radiation sensitivity would be increased 40 to 60 per cent. Expressed in terms of the Rubens linear pile, it is a fair estimate to rate the surface thermopile of bismuth silver (17 by 17 mm) at from 15 to 20 times the sensitivity of an iron-constantan thermopile. In such researches as can be performed with the thermopile inclosed and evacuated to 0.1 mm pressure (thus obviating the unsteadiness caused by air currents) the sensitivity attainable is at least twice this value. In fact high precision work can not be done with these instruments in open air; and hence the inclosing vessel might as well be one that may be evacuated, thus doubling the sensitivity.

From the data just cited, it may be seen that when the three units were connected in series the internal resistance was about 6.4 times the external (galvanometer) resistance; and the radiation sensitivity was about two-thirds that of the thermopile having the units joined in parallel, and having a resistance of 3.8 ohms. From this it appears that the external resistance may be considerably different from the internal resistance without seriously affecting the radiation sensitivity.

Obviously, the sensitivity to be attained depends upon the number of units, and this depends upon the skill and patience one has in constructing such instruments. From the tests made thus far, there appears to be a small permanent emf (resulting probably from the difference in emissivity of the hot and the cold junctions), but it causes no annoyance other than displacing the galvanometer deflection several centimeters on closing the circuit. In the linear pile this is obviated by having the two sets of junctions covered with receivers which are suspended in air.

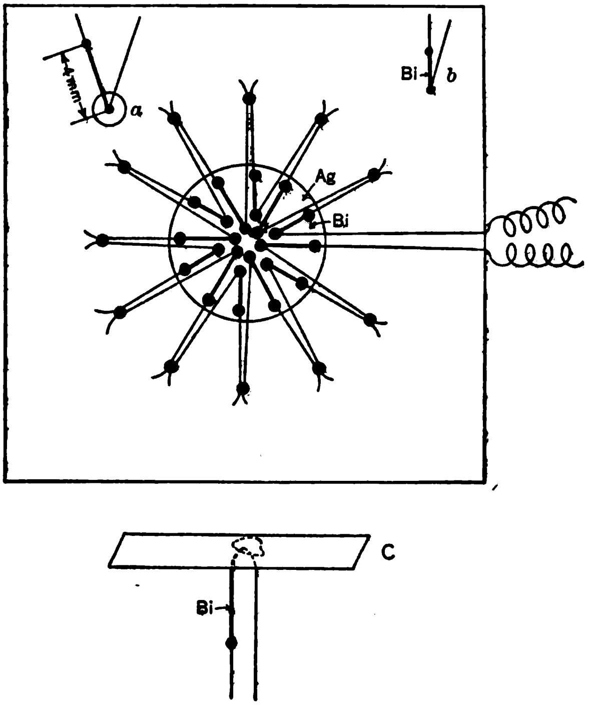


Fig. 7

In Fig. 7 is shown a point source (receiver) thermopile which is useful in measuring radiation confined in a small circular area. The individual junctions (Fig. 7, a) are made by attaching a small bead of tin to the silver wire, hammering it thin (1 mm diameter), fusing the bismuth wire thereto, painting the rear side with shellac, blackening the front side, and then mounting the same (overlapping) upon a sheet of mica having a central opening 1 cm in diameter. This thermopile consists of 16 elements joined in series, and has a resistance of 10 ohms. The central pile of receivers presents a continuous surface 4 mm in diameter. Mounted as a photometer, this instrument may be used in comparing the intensities of light sources.

Another point receiver thermopile of 10 elements, suitable for star images, sun spots, etc., was constructed of bismuth wire 0.04 mm and silver wire 0.019 mm diameter. The fine wires were made, from the material previously described, by reduction in nitric acid. The receivers were constructed as shown in Fig. 7, b the active junctions being insulated with a thin coat of shellac. Back of these junctions, but not in metallic contact with them, was placed a disk of tin 1 mm in diameter and 0.01 mm in thickness. The rear side of this disk was left bright; and the front side, including the active junctions, was covered with the lampblack and platinum black combination already described. The active junctions occupied only a portion of the disk. The resistance (tested before and after the junctions were placed in contact with the disk) was 19.3 ohms. The bismuth wires were 3 mm long, but for weak sources, such as star images, the length of the bismuth wire could be reduced to 2 mm, thus reducing the resistance to about 12 ohms. When used with a gavlanometer of 5.3 ohms resistance, half period of 3.5 seconds and sensitivity of 2×10^{-10} ampere, the deflection for a standard sperm candle and scale at 1 m was from 61 to 62 cm. From the experiments described on a previous page, this value should be increased from 20 to 25 per cent, owing to the difference in resistance of the thermopile and the galvanometer. In practice one would provide a more suitable galvanometer, and the deflection would therefore be 75 to 76 cm per meter candle.

The Nichols radiometer, used for measuring heat from stars, gave a deflection of 52 cm per meter candle when used on a complete period of 11 seconds. A magnetically shielded galvanometer is easily operated with this or even a greater period; and since thermopiles and radiomicrometers of the abovementioned sensitivity should be operated in inclosures exhausted to 0.1 mm pressure, which doubles the sensitivity, it appears feasible to produce a radiometer having at least 4 times the sensitivity previously employed in measuring the radiation from stars.

Point receivers of this type would be useful in radiation pyrometers (Fery's) which are now made with but one thermo element.

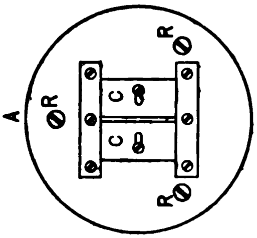
These surface thermopiles, built as they are on a small scale, foreshadow the possibilities which the future may bring forth in the form of large receiving surfaces, similar in principle but of somewhat different design, which, by utilizing (solar) radiation, will generate sufficient current to operate relays, recording devices, etc.

By placing a surface thermopile (single unit of 20 or more junctions) back of the manganin heater in an Ångström pyrheliometer, but not in contact with the heater, as now obtains, it is hoped to obtain a more reliable instrument for measuring radiation in absolute measure.

In Fig. 8 is shown a double-walled case for a (linear) thermopile. It is modeled after the bolometer case described in the previous paper, and consists of three parts: (1) The tube with diaphragms, (2) the main double-walled jacket, and (3) the end piece which supports the thermopile from three rods, R. The latter may be rotated about a horizontal axis to adjust the thermopile slit upon a spectral line, and then is clamped by the nuts, K. The metal disk, Fig. 8, A, supports the adjustable slit, c, c, and the thermopile, T.

For adjusting the slit upon a spectral line, the eyepiece, with a right-angled prism, is pushed down in front of the slit; the fine adjustment being made by means of a micrometer screw, S, which rotates the case about the screw, D, as an axis. Experiments show that unless the water supply is of uniform temperature it is better to have it stand in the jacket surrounding the radiometer rather than to have it flowing. In this laboratory it has been found sufficient to use a double-walled jacket containing an air space about 1 cm in thickness.

The sensitivity of a surface bolometer varies as the square root of its surface. The aforedescribed linear thermopiles have practically the same sensitivity as linear bolometers, but their surface sensitivity does not follow the square-root law, there being an optimum value which, on the dimensions tested, was 20 per cent



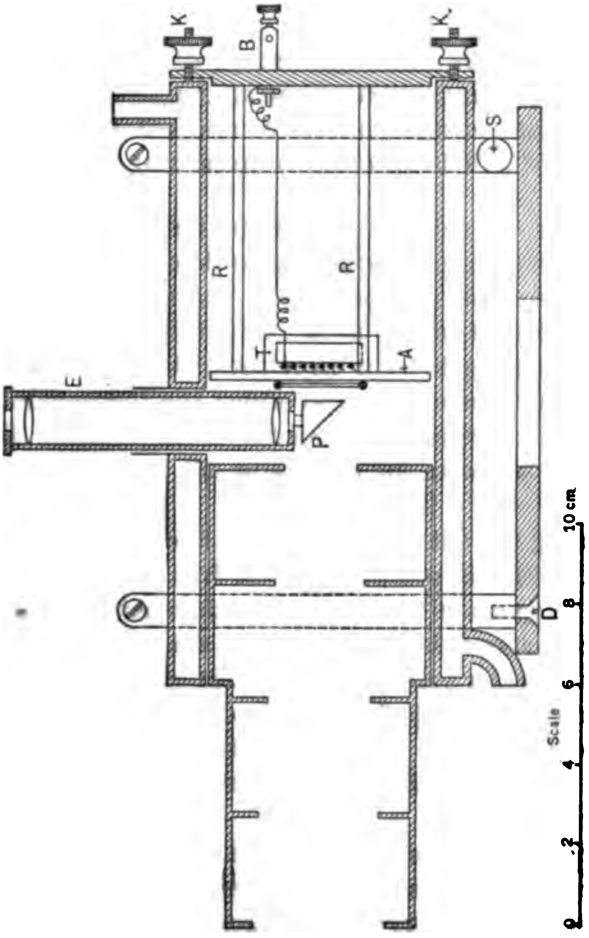


Fig. 8

greater than the square-root law. Hence, if one has the patience to construct such an instrument it seems possible to obtain a surface thermopile which has a higher sensitivity than a surface bolometer. Unfortunately at this writing no good surface bolometers were at hand to make this comparison.

(*c*) **Thermopile-Galvanometer Sensitivity Testing Device.**—In places where the galvanometer and (air) thermopile can be kept at a uniform temperature it is most convenient to test the galvanometer sensitivity by passing a known current through it. For this purpose it is desirable to have the galvanometer connected with the thermopile by means of a two-way switch. This enables the operator to throw the switch at will from the thermopile circuit to the battery circuit. When the galvanometer is adjusted to a high sensitivity this operation may seriously displace the zero of the scale reading. It is therefore desirable to test the galvanometer with the thermopile circuit closed. For this purpose an auxiliary coil of wire is placed in a fixed position near the galvanometer coils through which a known current is passed. This will cause a deflection which is proportional to the current sensitivity of the galvanometer. The relation of the current sensitivity of the galvanometer to the sensitivity as defined by this arbitrary standard may easily be determined by passing a known current through the galvanometer coils. If the thermopile is used in vacuo, a standard source of radiation should be used in testing the sensitivity.

In conclusion, it is desirable to add a word of caution in regard to the use of these surface thermopiles, for we are confronted with a difficulty not usually encountered, viz, a possible drift[24] of the galvanometer if the thermopile is not well shielded and the shutter is not kept at a uniform temperature.

It is therefore important to have the hot and cold junctions of the same emissivity and heat capacity. To this end it seems advisable to attach "receivers" to both the hot and the cold junctions. To the latter the receivers may be attached by means of low melting point (Wood's) alloy, shellac, or an amalgam such as used by dentists, after the instrument is completed.

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[24] A surface bolometer is subjected to the same disturbances, in addition to air currents caused by the heat generated by the battery current, but the drift can be balanced by means of a slide wire.

The quickest way to balance the drift in the thermopile circuit is to alter the position of a magnet placed near the galvanometer, the sensitivity being tested, as already mentioned, by an auxiliary coil placed on the galvanometer. Another method for keeping the galvanometer reading adjusted would be to place a coil of wire near the galvanometer and pass a current through it in the proper direction to cause a deflection in the opposite direction to that caused by the drift of the thermopile. By varying the distance of the coil from the galvanometer or the current through the coil, or both, a balance may be brought about just as in the surface bolometer. Not having as yet experienced any of these difficulties in this laboratory, these suggestions are given in anticipation of what may be encountered by others whose problems may not admit of thorough protection of the thermopile from temperature variations.

IV. THE BOLOMETER WITH ITS AUXILIARY GALVANOMETER[25]

In the present paper only the most important of the recent improvements of this instrument are discussed. Until recently the notion prevailed that the bolometer, in vacuo, is difficult to operate; but the advances made during the past few years indicate that, whenever the investigation admits of it, bolometers, and in fact all the aforesaid radiometers, should be operated in a vacuum of not more than 0.1 mm mercury pressure.

1. HISTORICAL SUMMARY

One of the recently described galvanometers is Paschen's,[26] which, for a period of 10 seconds and a resistance of 1 ohm, has a sensitivity of about 2.5×10^{-10} ampere.

Nichols and Williams[27] have described a convenient galvanometer with an excellent magnetic shield. The galvanometer had 4 coils of wire, each 2.6 cm diameter. Each coil was wound in 3 sections; 81 cm of No. 38, 328 cm of No. 32, and 1318 cm of No.

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[25] The notes on the auxiliary galvanometer are given in Appendix I.

[26] Paschen: Ann. der Phys. (4), 33, p. 738; 1910.

[27] Nichols and Williams: Phys. Rev., 27, p. 250; 1908.

26 wires; resistance, 5.6 ohms (1.4 for the 4 coils in parallel). The magnet system consisted of two groups of 7 needles each, of tungsten steel wire 0.165 mm diameter and 2 mm long. The sensitivity was 4×10^{-10} volt for 1 mm deflection for a complete period of 6 seconds. Of chief interest are the cylindrical shields of silicon steel, which had a shielding ratio 40 times as great as the best form designed by Du Bois and Rubens. Using 3 of these shields, designed according to the computations of Wills,[28] the "shielding ratio" was 2903 for the unannealed, and 4274 units for the annealed cylinders. Five shields of soft-iron water pipe gave a shielding ratio of 2725, and with a later design 6 shields of annealed water pipe gave a shielding ratio of over 9000.

Trowbridge [29] has used a similar outfit including a vacuum spectrobolometer, in which the bolometer and the optical parts of the spectroscope are evacuated.

Seddig [30] has described an "absolute bolometer" in which two branches have a positive and two branches have a negative temperature coefficient. He uses iron and carbon for the branches. The novelty in the device is the use of carbon and the exposure of the four branches to radiation, but, from tests made on the commercial instrument, it does not seem to justify the claims made for it. The iron is of course too short lived, owing to oxidation, and the "absolute" measures can be made only after calibration against a known source of radiation. In this respect all instruments may be calibrated to read in absolute units.

Leimbach [31] has used extensively a linear "absolute bolometer" constructed on the double-bridge principle described by Paalzow and Rubens.[32] The area of the bolometer strips was 0.63 mm^2 (two strips 0.025×12 mm), resistance 165 ohms, and thickness 0.00028 mm. He used an Edelmann string galvanometer, the sensitivity of which was 7.4×10^{-10} amp. In the radiation sensitivity test he used a Du Bois-Rubens galvanometer having a period of 10 seconds. (The current sensitivity was not given.) The deflection was about 200 cm for a candle and scale at 1 m, which is a high sensitivity.

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[28] Wills: Phys. Rev., **24**, p. 243; 1907.

[29] Trowbridge: Phys. Rev., **27**, p. 282; 1908. Phil. Mag. (6), **20**, p. 768; 1910.

[30] Seddig: Phys. Zs., **10**, p. 533; 1909. Ver. Phys. Gesell., Berlin, **13**, p. 53; 1911.

[31] Leimbach: Zs. für Wiss. Photogr., **7**, p. 152; 1909. Ann. der Phys. (4), **33**, p. 308; 1910.

[32] Paalzow and Rubens: Ann. der Phys. (3), **67**, p. 529; 1899.

Warburg, Leithauser, and Johansen[33] have made important contributions to the study of vacuum bolometers, and their complete paper should be consulted. They studied bolometers varying from 0.2 to 1.0 mm in width, and found that in the vacuum bolometer the heat lost by radiation is proportional to the third power of the temperature. In a vacuum bolometer the maximum radiation sensitivity is proportional to the square root of the width of the bolometer, while for an air bolometer the sensitivity is proportional to the width. The heat lost by air conductivity for a bolometer 1 mm wide is 4.5 times, and for a bolometer 0.2 mm wide it is 14.8 times as great as the loss by radiation. The internal heat conductivity reduces the radiation sensitivity of an air bolometer by 15 per cent and that of a vacuum bolometer by 38 per cent.

The radiation sensitivity of a vacuum bolometer was found to be proportional to the current for small values, but for a large current the radiation sensitivity of a narrow bolometer passes through a maximum. This maximum is attained for a current density at which the radiation sensitivity of the air bolometer does not depart appreciably from proportionality with current. A vacuum bolometer 0.2 mm wide was found to be 10 times as sensitive as it was in air, when used in a small current, but only 5 times as sensitive when in both cases the current was raised to its highest operating value. This is of practical importance when one is limited to a given galvanometer sensitivity.

The manner in which the radiation sensitivity varies with the gas pressure and with the bolometer current is well shown in Fig. 9 which is taken from a paper by Buchwald.[34] In this illustration the ordinates represent the galvanometer deflections when the bolometer was exposed to a source of radiation. The various curves represent different gas pressures. In this experiment the bolometer was 0.15 mm wide. Using a bolometer 0.5 mm wide the curves (see Fig. 11) do not come to such a sharp maximum as the ones shown in Fig. 9.

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[33] Warburg, Leithauser, and Johansen: Ann. der Phys., **24**, p. 25; 1907.

[34] Buchwald: Ann. der Phys. (4) **85**, p. 928; 1910.

2. THE CONSTRUCTION OF SENSITIVE BOLOMETERS

In the bolometer the sensitiveness is closely proportional to the square root of the surface, so that in spectral energy work, where the bolometer strip is narrow, the sensitiveness attainable through the bolometer is limited.

Since writing the previous paper the present instrument has been considerably changed, and the experience gained indicates that in air bolometers it is not advisable to use platinum which is much less than 0.001 mm in thickness. The methods of mounting are as before described. In mounting the bolometer strips on the holder, the one exposed to radiation is first soldered in place, using rosin for a flux. The unexposed strip is made a little longer, so that it will have a slightly greater resistance, which by subsequent resoldering is made equal ro that of the exposed strip. This is a difficult task when using very thin bolometer platinum. In one of the latest bolometers (No. 9; 0.0003 mm thickness) consisting of platinum strips 10 by 0.6 mm, the resistance of the exposed strip is 6.447 ohms and of the unexposed strip is 6.459 ohms. But the risk of breaking is too great to balance to such a nicety

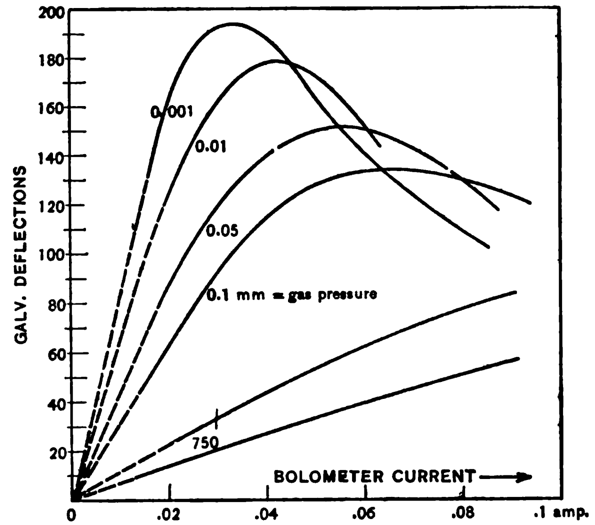

Fig. 9

and in the vacuum bolometer, known as No. 10, to be described presently, the bolometer strips are balanced to 1 per cent.

The question of a satisfactory slide wire for balancing the bolometer has required considerable attention. It was found that the constantan slide wire became soiled and required frequent polishing. In the latest design of vacuum bolometer the mercury contact previously described is used in connection with slide wires of platinum which are 0.5 and 1 mm in diameter.

3. COMPARISON OF SENSITIVENESS OF VARIOUS BOLOMETER-GALVANOMETER COMBINATIONS

Important data on sensitive radiometers, and particularly that relating to bolometers, were given in Table IV of the previous paper. It will be noticed that the bismuth-silver thermopile is as sensitive as the air bolometer. In the previous paper it was shown that the temperature sensitiveness of the various instruments falls in two groups. To the first group belong the earlier instruments of Rubens, of Snow, and of Paschen, with a sensitiveness of about 5×10^{-5} degrees per mm deflection. To the second group belongs a more sensitive combination of Paschen's and the writer's vacuum bolometer, in which 1 mm deflection corresponds to a rise in temperature of $5° \times 10^{-6}$ and $7° \times 10^{-6}$, respectively. In other words, the instruments of the latter group have the same sensitiveness, and any increase is to be attained by lengthening the scale distance. The bolometer current of 0.04 ampere is about the maximum limit for accuracy. The sensitiveness of the writers' instruments could have been further increased by lengthening the scales distance to 2 m, when the temperature sensitiveness would have been $3°.5 \times 10^{-6}$, and by doubling the galvanometer period, when the sensitiveness would have been $1°.7 \times 10^{-6}$ against Paschen's $1° \times 10^{-6}$. Such a computation is of course somewhat illusory because of a difference in the galvanometer damping, and in the *radiation sensitivity* which is higher in a vacuum. On actual trial (using the 10-magnet system just quoted) for a full period of 20 seconds the sensitiveness of one of the writer's galvanometers was 7×10^{-11} ampere and on 30 seconds it was 3.7×10^{-11} ampere.

4. CONSTRUCTION OF A VACUUM BOLOMETER

A convenient vacuum chamber was made by combining the hemispherical mirror, *m*, with a small glass cup as shown in Fig. 10. The opening in the mirror is covered with a fluorite window, *f*, which is attached with cement. The glass window, *w*, admits viewing the inclosed bolometer strip for adjusting it in the spectrum. The exhaust tube, *t*, leads out along the axis to the rear of the bolometer case where it is joined (in series with a large, 4-liter, glass bottle to give it capacity and thus avoid variation in gas pressure) to a Geryk oil pump. The slate support of the bolometer strips, *b'*, *b'* (see Figs. 12 and 13 of the previous paper), is placed within this glass chamber, and the battery, shunt, and galvanometer wires, properly insulated, are inserted through the short tubes, *l*, and soldered directly to the terminals of the bolometer strips. All these joints are closed with a cement made of rosin and pure rubber which has a low vapor pressure. The exposed bolometer strip is brought in the focus of the hemispherical mirror by removing the microscope, E (Fig. 12 of previous paper), and reflecting sunlight along the axis of the bolometer from the rear. For this purpose the heavy battery current wires, which are the support of the bolometer holder, are of the proper length and flexibility to admit of such an adjustment. Two of the three sets of lead wires are illustrated in position in Fig. 10. The bolometer strips are 10 by 0.6 mm and have a computed thickness of 0.0003 mm and resistances of 5.604 ohms (exposed strip) and 5.664 ohms, respectively. The resistance of the complete bolometer is about 8.9 ohms (depending, of course, upon the battery current and the vacuum) with a temperature coefficient of 0.0230 ohms per degree. The resistance of the galvanometer is 5.09 ohms at 20° C, with a temperature coefficient of 0.0194 ohms per degree.

The rear side of each bolometer strip is left bright, and the front side is painted with a mixture of equal parts of lampblack and of platinum black, which is made into a smooth, thick, paste with turpentine, or with a dilute alcoholic solution of shellac. This is applied with a brush made of a thin strand of a fine silk thread. By starting at one support and by making one uniform stroke along the bolometer strip, and not stopping until after arriving at

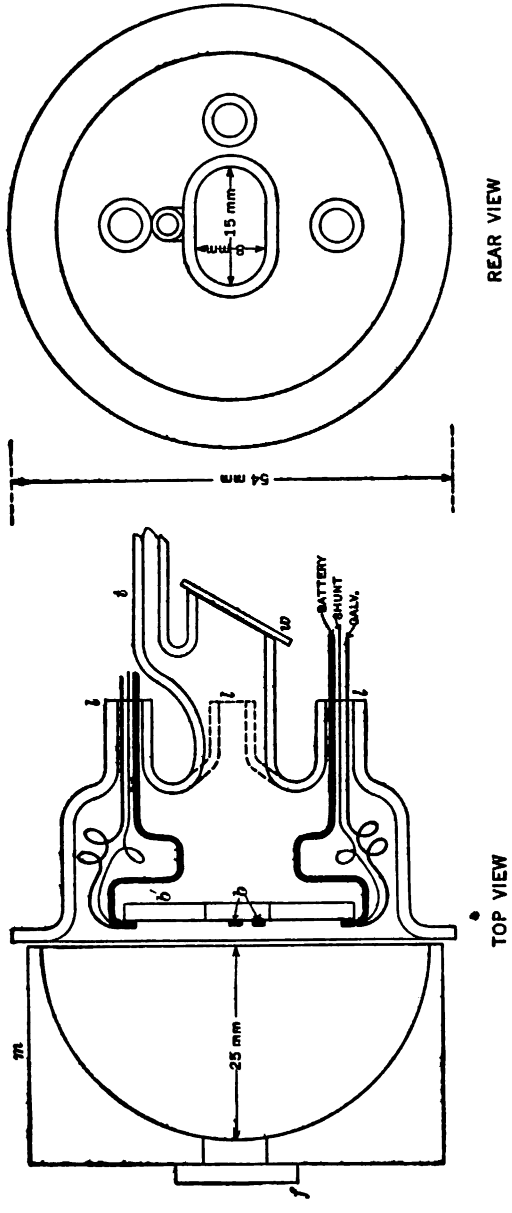
15 mm
8 mm
REAR VIEW
54 mm
t
w
BATTERY
SHUNT
GALV.
l
l
l
b'
b
TOP VIEW
25 mm
m
f

Fig. 10

the other end, there is no danger of tearing the strip. After this, the bolometer is blackened a little more by smoking over a candle flame. Chemically precipitated platinum black should be used instead of the powdered electrolytic material because it is blacker. However, a layer of platinum black, if successfully deposited electrolytically upon a bolometer strip, is the best of all.

The degree of evacuation is measured by means of the length of the cathode dark space in a small vacuum tube having disk electrodes of aluminum. There is practically no leakage when the stopcocks are in good condition and the vapor pressure from the cement is a fairly constant value, so that a cathode dark space of 2 mm (white CO_2 glow of hydrocarbon vapors) is easily maintained for weeks. The radiation sensitivity is lower for hydrocarbon vapors than for nitrogen or hydrogen, so that in practice air is admitted and the hydrocarbon vapors are pumped out. For example, starting with the bolometer after it has stood for some days at 0.2 mm pressure, when the hydrocarbon vapors predominated, the radiation sensitivity was doubled by admitting air and exhausting to the same pressure.

In practice, the sensitivity is varied by introducing resistance in series with the galvanometer. It is therefore necessary to determine the resistance of the bolometer with considerable accuracy, for different gas pressures, and for different values of battery current. As illustrated in Fig. 11, the resistance of the bolometer is practically constant for gas pressures as low as 0.2 mm. This degree of evacuation is sufficient to eliminate the effects of air currents, but the radiation sensitivity is not increased to a marked extent until a much lower vacuum is attained. This is illustrated in the upper part of Fig. 11, from Buchwald,[35] which shows the increase in sensitivity (the ordinates, which are the galvanometer deflections arising from exposing the bolometer to a constant source of radiation) with decrease in gas pressure; and also with increase in current. In this experiment the bolometer strip was 0.2 mm wide. In Fig. 9 using a bolometer strip 0.15 mm wide, the radiation sensitivity increased at a more rapid rate with decrease in gas pressure.

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[35] Buchwald: Ann. der Phys. (4), 33 p. 928; 1910.

In the present bolometer the radiation sensitivity was doubled by reducing the gas pressure from 760 mm to 0.1 mm (6 mm cathode dark space). In hydrogen at 0.1 mm the bolometer was 2.5 as sensitive as in air at 760 mm pressure. With a Geryk oil pump a vacuum of 0.015 to 0.02 mm can be produced, when the radiation sensitivity is much higher. The sensitivity of this bolometer in air with the fluorite window in place was tested with a standard sperm candle placed at a distance of 2 m (an ordinary paraffin candle gives 10 to 12 per cent higher values). The fluorite window, which was flawless and 3 mm in thickness, transmitted about 93 per cent of the radiation from a sperm candle. The battery current was 0.03 ampere. Using a galvanometer period of 10 seconds and a sensitivity of 1.4×10^{-10} ampere, the mean value of the deflection was 30.1 cm, or 120 cm (129 to 130 cm when corrected for losses in the fluorite window) with a candle at a distance of 1 m, so that as ordinarily used, when evacuated to 0.1 mm pressure, the equivalent deflection would be at least 280 to 300 cm. Under these conditions an accuracy of 1 part in 200

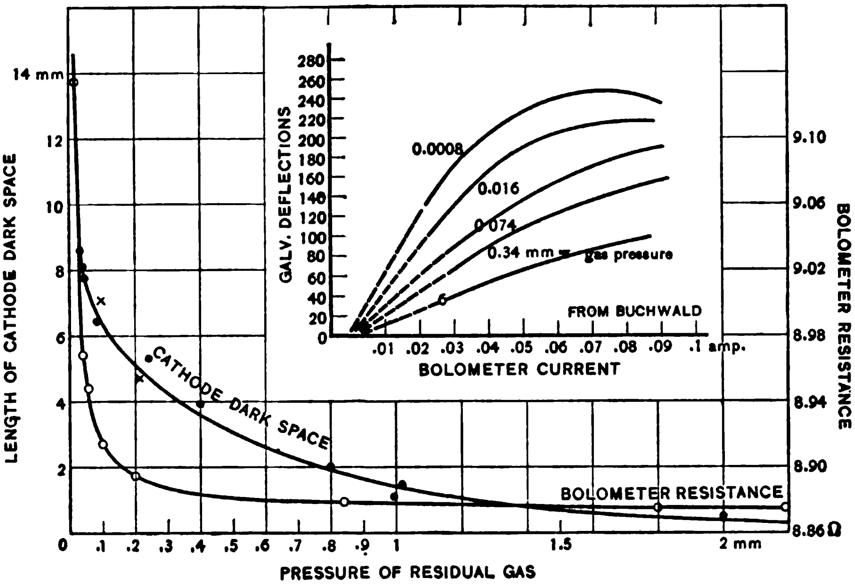

Fig. 11

to 400 is easily attained. In measuring weak radiation, the sensitiveness could be increased to at least 650 to 700 cm deflection by increasing the scale distance to 1.5 m, the galvanometer period to 12 seconds, and the battery current to 0.04 ampere, but keeping the pressure at 0.1 mm. By using the scale at 1.5 m, using a complete period of 12 seconds and a battery current of 0.03 ampere, but evacuating the bolometer to 0.01 mm or less, the radiation sensitivity would be increased two to three fold (600 to 900 cm). In qualitative work it is of course possible to use a higher sensitivity by using a large battery current, but in this bolometer the galvanometer deflection becomes unsteady when the battery current is higher than 0.04 ampere.

5. ELECTRIC BATTERIES FOR BOLOMETERS.

The general complaint against the bolometer is its "drift" caused by a gradual drop in the battery voltage or variation in bridge current.

While the bolometer is usually spoken of as being "simply a Wheatstone bridge," it is sometimes forgotten that, from the very nature of the construction of the bolometer, difficulties must be expected in operating it. A Wheatstone bridge is constructed of wires having a negligible temperature coefficient. In a bolometer two branches of the bridge are purposely constructed of metals having a high temperature coefficient of resistance. These two branches are made as symmetrical as possible in order that, when not exposed to radiation, they will be equally affected by temperature variations. But it is impossible to cut bolometer strips of the same width and mount them so that they will have the same resistance and the same radiating surface (emissivity). Hence, if the battery current varies, the resistance of one branch of the bolometer will vary more than the other and the bridge becomes unbalanced. One of the best balanced and most sensitive bolometers (the vacuum bolometer, already described) ever mounted by the writer would change in resistance so much that for a variation of $\frac{1}{1\,000\,000}$ ampere, the bolometer would be unbalanced by 1 mm. Of course, in the actual work the fluctuations in the deflections are greater than 1 mm. Formerly the writer operated his bolometer on a portable storage battery which for several days after charging would give a sufficiently constant voltage so that there was no drift. Occasionally the galvanometer needle would vibrate when on shaking the storage cell (supposed to liberate the gas bubbles) or on substituting a new cell, the difficulty would be overcome. From this the writer concluded that the fault was with the battery. During the past two years he has used a large plate (single cell) battery of 400 ampere hour capacity, situated in a basement room (at uniform temperature) and has had no difficulties whatever from this source. The only fluctuations that arise are caused on windy days by air currents in the galvanometer, and in humid weather by grounding through the bolometer circuit.

Hulett[36] has described a battery which is really an enlarged form of cadmium sulphate cell. The cell gives good results while it lasts, but appears (in spite of its constancy) never to have given the satisfaction in bolometric work that was supposed to obtain when it was first described. On the other hand, the cell of large capacity (400 ampere hours) can be operated on a small battery current (0.03 in the writer's work) without variation in voltage. In actual practice, on standing over night, the unbalancing of the bolometer never amounts to more than 1 or 2 cm; usually it amounts to only a few millimeters and this is probably owing chiefly to a change in temperature and in the vacuum.

6. RADIATION SENSITIVITY OF DIFFERENT PARTS OF A BOLOMETER STRIP

Johansen[37] using a bolometer strip 11 mm long, 0.54 mm wide and 0.001 mm thick, found the sensitivity of different parts of the same when exposed to a standard source of radiation. For this purpose he projected (crosswise) an image of a Nernst glower upon different parts of the bolometer and noted the galvanometer deflection. At the ends, Fig. 12, the deflection is practically zero owing to loss by heat conduction. The errors resulting therefrom will be negligible when comparing sources of radiation which do not differ greatly in intensity. When the sources differ greatly in intensity, as for example, different parts of a spectral energy curve, the error may be avoided by reducing the incident energy from the intensest source by means of a sectored disk. In the writer's vacuum bolometer the thickness of the strips is only about one-third that used in the above experiment. The loss by conduction from the ends is, therefore, much smaller and the sensitivity curve is flatter than that given in Fig. 12. The loss by conduction from the ends is further reduced by having the incident radiation cover only about two-thirds of the bolometer strip.

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[36] Hulett: Phys. Rev., **27**, p. 33; 1908.

[37] Johansen: Ann. d. Phys. (4), **33**, p. 517; 1910.

V. SELECTIVE RADIOMETERS

The well-known fact that the resistance of selenium changes, when exposed to the light, has been applied to photometric measurements. Pfund[38] has shown that the maximum sensitivity of the selenium cell is at about $\lambda = 0.7\ \mu$. According to Stebbins[39] some cells have two maxima, at 0.586 μ and 0.694 μ, respectively. If an alloy could be produced which has its maximum sensitiveness (i. e., its resistance change greatest) for those wave lengths to which the eye is most sensitive, it might be possible to devise a method for measuring radiant efficiencies, without the use of an absorption

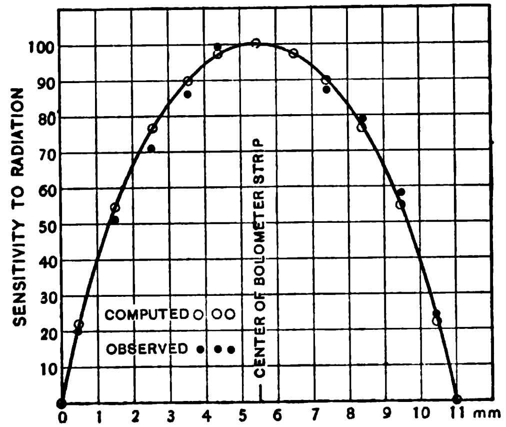

Fig. 12

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[38] Pfund: Phil. Mag. (6), 7, p. 26; 1904. From his latest work (Washington Meeting, Amer. Phys. Soc., Dec. 27, 1911, Phys. Rev., 34, p. 370, 1912), it appears that the position of maximum sensitivity varies with the intensity of the incident light so that the selenium cell does not appear to be a promising instrument in photometry or radiometry.

[39] Stebbins: Astrophys. Jour., 27, p. 138; 1908.

screen or a spectrometer, as now used for separating the visible from the infra-red.

In the ultra-violet the photo-electric effect has been applied by Küch and Retschinsky to measure the radiation from the mercury arc.[40] Little is known in regard to this class of radiometers. Since they are highly selective their application is limited, but if the proper combination could be found having a sensitivity curve similar to the eye it might be applicable in some special classes of photometric and radiometric work. If the transformation of radiant energy were as complete in the photo-electric effect as in a bolometer it would be a useful instrument, since it does not appear to be subject to such perturbations as is the bolometer. However, from the data at hand, especially that relating to the selenium cell, this type of radiometer does not appear to merit much of the attention that should be devoted to the further improvment of radiation instruments.

For determining the spectral energy distribution of weak and intermittent radiations, such as the flashes of light from the firefly, a species of spectro-photographic photometry has been employed [41] with considerable success. A "panchromatic" plate was used. The procedure consisted in photographing the spectrum of the light of the firefly and that of a standard lamp, after which the "densities" of the negatives were compared photometrically. The spectral energy distribution of the standard lamp was determined with a bolometer and from this the spectral energy curve of the light of the firefly was determined by multiplying the energy values of the standard glow lamp by the ratio of densities (firefly light ÷ glow lamp light) at each wave-length. The advantages of this method are, first, that all portions of the spectrum are recorded simultaneously, so that unsteadiness of the total light is permissible; and, second, that the plate is integrative, so that the obstacles imposed by low intensity may be overcome by long exposure.

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[40] Küch and Retschinsky: Ann. der Phys. (4), **20**, p. 563; 1906.

[41] Ives and Coblentz: This bulletin, **6**, p. 321, 1909. Coblentz: Canadian Entomologist, p. 355, Oct., 1911; Carnegie Publication No. 164, 1912. Pierce: Phys. Rev., **30**, p. 663, 1910 (Fluorescence Spectra).

VI. A NEW FORM OF RADIOMETER

In the previous paper[1] a combination of the Boys radiomicrometer and the Nichols radiometer was described. The experiments showed that the combination is feasible,[43] but the time has never been opportune to continue the experiments to determine the proper dimensions of the suspension and the field strength of the magnets to attain the maximum radiation sensitivity. Bismuth was previously employed in the thermojunction; but it now appears that a short fine wire of constantan might prove more satisfactory, because it is not so diamagnetic.

Another type of radiometer (at least a type of radiation detector) suggests itself by taking advantage of the change in astaticism, caused by flexure of the vane joining a pair of suspended magnets. On a previous page it was shown that the change in astaticism of the galvanometer suspension was overcome by attaching the magnets with a cement which is not hydroscopic. This condition may be reversed, by joining two magnets by means of thin rectangular sheets of material having a high coefficient of expansion (e. g. ebonite) as shown in Fig. 13, A. The upper horizontal steel bar (dimensions 8 by 0.3 by 0.08 mm) is attached to a short glass rod which carries the mirror. The (vertical) vanes are painted black. Two vanes are used for symmetry, but only one is exposed to radiation. The bars are magnetized before mounting, and astatized after the suspension is completed just as is done with an ordinary galvanometer magnet system. In Fig. 13, B, is given a similar combination of fine steel wires joined together by means of light vanes, which takes the place of the vanes in an ordinary Nichols radiometer. This latter combination has not yet been tested to determine its utility. Some preliminary experiments were made on a pair of astatized magnets

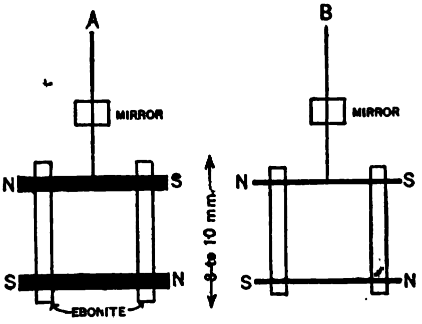

Fig. 13

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[43] This Bulletin, 2, p. 479, 1906.

joined with radiation vanes (receivers) of blackened mica, and suspended in a glass tube by means of a quartz fiber. The earth's field controlled the equilibrium position of the system. In practice, of course, control magnets would be used as in galvanometers. When one vane was exposed to radiation there was an appreciable deflection. The experiment showed that the vane must be light (of low heat capacity) so that it will come to a thermal equilibrium in a short time. Furthermore the experiment showed that this method of measuring radiation, by changing the astaticism of a magnet system by flexure of the magnets, is feasible. Whether it will prove more sensitive than the more complicated radiometers herein described remains undetermined. The sensitiveness will depend, in part, upon the astaticism of the pair of magnets, upon the strength of the controlling field, and upon the length of the magnets. The investigation of these questions may require considerable time before it will be possible to report on the merits of this type of radiometer.

VII. SUMMARY

The present paper deals with four instruments for measuring radiant energy, viz, the radiomicrometer, the linear thermopile, the Nichols radiometer, and the bolometer with its axuiliary galvanometer.

As a result of this historical inquiry and by experiment it is shown that the radiomicrometer is capable of great improvement by reducing its weight, by lengthening its period, and by placing it in a vacuum. It was shown (in a previous paper) that on account of para- and dia-magnetism the sensitiveness of the short period radiomicrometer is limited to perhaps only one-half that of the best vacuum bolometers described. The instrument is free from magnetic disturbances which permits the use of a longer period; and by placing it in a vacuum of 0.1 mm or less pressure its sensitivity is comparable with that of a good bolometer. By properly shielding it from sudden changes in temperature and by using a long period the sensitivity of this instrument should excel all the other types.

It was shown that the Rubens thermopile is only about one-half as sensitive as a bolometer; but it can be greatly improved by using thinner wires (0.06 to 0.08 mm diameter) and by using the instrument in a vacuum. The computed errors, due to the Peltier effect, are about 1 part in 300. The thermopile is not so well adapted as is the bolometer for instantaneous registration of radiant energy, and it does not admit so great a range in variation of sensitivity, but on account of its greater steadiness it commends itself for measuring very weak sources of radiation, e. g., the extreme ultra-violet and infra-red region of the spectrum.

A thermopile of bismuth-silver is described. It is easily constructed, and its sensitivity is from 2.5 to 3 times that of the iron-constantan pile. A surface thermopile is also described, the radiation sensitivity attained being six-sevenths the theoretical value.

By a direct comparison it was shown in a previous paper that the Nichols radiometer can be made just as sensitive as the bolometer, but its period will be much longer. It was found that the Nichols radiometer is not selective in its action, and hence that it can be used for measuring ultra-violet radiation. The main objection to the use of a Nichols radiometer is its long period, but since it is easily shielded from temperature changes and since it is not subject to magnetic perturbations, this long period is of minor importance so long as we are dealing with a constant source of radiation. In spectral energy work its usefulness is limited to the region in which the window is transparent. The fact that the Nichols radiometer deflections can not be obtained in absolute measure is a minor objection, since in but few cases thus far at least has it been necessary to thus obtain the deflections. The action of a Nichols radiometer is somewhat analogous to a photographic plate in that it will detect weak radiation, provided one can wait for it, and on account of its great steadiness is, of all the instruments considered, probably the best adapted to search for infra-red fluorescence.

A bolometer installation is so distributed that it is difficult to shield from temperature changes. In spite of its small heat capacity the bolometer has a "drift" due to a slow and unequal warming of the strips. Air currents which result from the hot bolometer strips also cause a variation in the deflections of the auxiliary galvanometer. Nevertheless, despite these defects, it is the quickest acting of the four instruments considered and is the best adapted for registering the energy radiated from a rapidly changing source. For precision work it is necessary to keep the bolometer balanced to less than 1 cm deflection.

A vacuum bolometer is described, and data given showing that it is the quickest acting, the most relaible, and the most sensitive of all the instruments described having a short period.

A storage battery is described which gives a constant current, thus overcoming "drift."

The auxiliary galvanometer is the main source of weakness in measuring radiant energy, and in places subject to great magnetic perturbations a period greater than 5 seconds, single swing, is to be avoided. Hence, although a greater sensitiveness is possible, the working sensitivity of the various galvanometers studied is of the order of 2×10^{-10} ampere (per mm deflection on a scale at 1 m). Under these conditions the various bolometers used were (as a fair estimate of the recorded data) sensitive to a temperature difference of 4×10^{-5} degree to 5×10^{-6} degree per mm deflection on a scale at 1 meter. The galvanometer sensitivity was found to be closely proportional to the period. Methods are given to avoid changes astaticism, and to provide effective magnetic shielding.

A direct comparison was made in a previous paper of the relative accuracy of the thermopile and the air bolometer in measuring intense and weak sources of radiation, and the results show that there is little preference other than a personal one in these two instruments.

The manner of reducing the sensitiveness of these instruments is of importance in precision work. The use of the rotating sectored disk for reducing the intensity of the source is liable to introduce errors which must be taken into account. A new form of rotating sector is described. (See this Bulletin, **7**, p. 249; 1911.)

It may be added that these tests were made in a building which is isolated from mechanical and magnetic disturbances, and hence under the most favorable conditions.

As a final remark it may be said that after four years of designing and testing various radiometers which were tried out on various researches, a bolometric outfit has been assembled which (while it is not of the highest attainable sensitivity) excels all the other herein-described radiometers for speed and accuracy. It consists of (1) a vacuum bolometer which is free from drift and which admits of quickly and accurately adjusting the sensitivity throughout a wide range; (2) a galvanometer of high sensitivity and well shielded magnetically. The suspension is well damped on 2.5 seconds swing, has sufficient weight not to be affected by earth tremors, is free from the usual changes in astaicism, and has a wide range of proportionality of deflection with current; and (3) a satisfactory storage battery.

NOTE I. THE CALLENDAR RADIOBALANCE

Callendar[43] has recently described an ingenious device in the form of a thermoelectric balance for the absolute measurement of radiation. It consists essentially in exposing a thermojunction, in the form of a disk, to radiation and compensating or neutralizing the consequent rise in temperature by the Peltier (cooling) effect which is induced by sending an electric current through the thermocouple. Another thermojunction in contact with this disk indicates the degree of compensation. In actual practice, in the disk form of radiobalance there are two disks, J_1 and J_2 (Fig. 14, B), into which are soldered iron and constantan wires. One of the vertical wires, P_1 or P_2, is joined to an electric battery while the terminals of the horizontal wires (Fig. 14, B) are joined to a d'Arsonval galvanometer. When either disk, J_1 or J_2, is exposed to radiation the galvanometer gives a deflection which is then neutralized by sending an electric current through P_1 P_1, or P_2 P_2. With a given instrument the intensity of the radiation which can be directly compensated in this manner by the heat absorption due to the Peltier effect is limited by the Joule effect, I^2 R, in the wires forming the thermocouple. In practice it is necessary to know (1) the area, A, of the aperture admitting the radiation, (2) the coefficient, P ($= \mathrm{T}d\mathrm{E}/dt$) of the Peltier effect in volts, (3) the current, I, through the couple, (4) the neutral current $\mathrm{I} = \mathrm{P}/\mathrm{R}$, giving neither heating nor cooling, and (5) the absorption coefficient, *a*, of the blackened surface of the disk. When the radiation is exactly compensated by the current, the intensity of the radiation, H, in watts per square centimeter is

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[43] Callendar: Proc. Phys. Soc., London, 23, Pt. I, Dec. 15, 1910.

$$aAH = PI - I^2R = PI\ (1 - I/I_0).$$

Callendar says "the chief disadvantage of the radiobalance is that the increase of the Peltier effect per 1° C for the couples employed is very nearly 0.0001 volt in 0.0150 volt." It is therefore necessary to read the temperature of the thermometer to 0°.1 C. It is also necessary to find the value of the neutral current at various temperatures. After these two calibration curves have been worked out it is a simple matter to expose either one of the disks to radiation, measure the compensating current with a milliammeter and read the thermometer, T, Fig. 14.

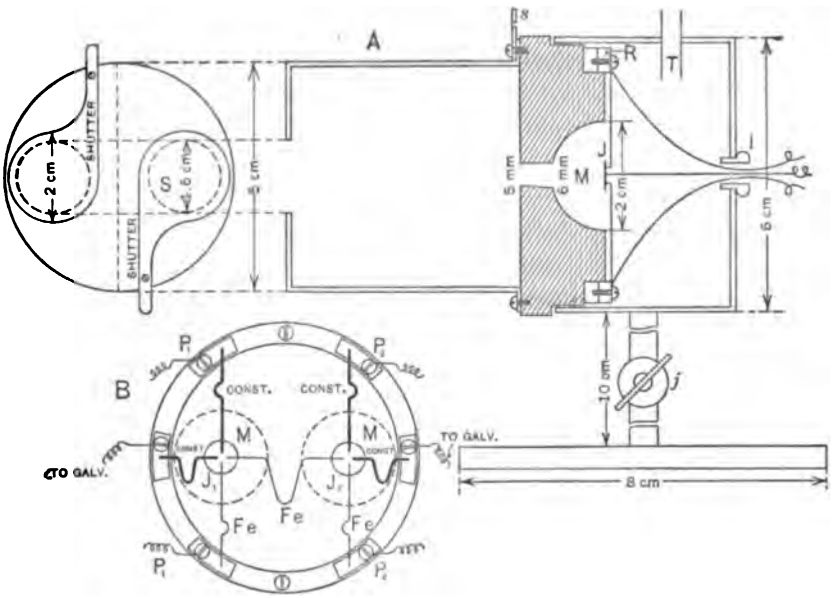

Fig. 14

Callendar has also described a cup radiobalance in which the receiver is in the form of a cup about 4 mm diameter which is a more complete absorber than the disk. In this instrument the compensation is measured by a series of thermojunctions which are insulated from the cup.

The cup form of radiobalance appeared to be more difficult to construct than the disk. In the design shown in Fig. 14, the writer therefore placed each disk J_1 and J_2, in the focus of a small hemispherical mirror, M, 2 cm diameter, cut in a thick piece of brass and then highly polished. The disks were 5 mm diameter and about 0.25 mm thick. The openings in the mirrors for admitting the radiation were 5 mm diameter, but they were covered with a metal plate having apertures 2.3 mm diameter in order to be able to compensate the maximum radiation from the sun, which in this locality amounts to about 0.12 watts per sq cm per second. The lead wires, P_1 and P_2, of constantan (0.3 mm diameter) and iron (0.2 mm diameter) were soldered close together into the disks on a circle about 3 mm diameter and the ends were soldered to copper blocks, P_1 and P_2 which were mounted upon an insulating ring, R, of fiber. This ring can be readily attached over the hemispherical mirrors. The front of the instrument was covered with a tube to exclude stray light and to hold the shutters S.

The neutral current depends, of course, upon the resistance of the lead wires. Experiments were therefore made by increasing the number of iron and constantan wires attached to each disk (in Fig. 14, B, they are indicated by a single wire) from 4 to 8 and the neutral current was raised from 0.4 ampere to 1.2 amperes. The last design (having 9 iron and 6 constantan wires in each disk and requiring a neutral current of 1.084 ampere for J_1 and 1.120 for J_2 at 25° C) was given a thorough test against a Callendar sunshine recorder which had previously been calibrated against the Abbot primary standard pyrheliometer. In the first test (5:26:'11) the solar constant as measured with the radiobalance was 5 to 6 per cent *lower* than the value observed with the sunshine recorder. It is to be noted that, as in the original calibration of the sunshine recorder used in the present tests, the instrument was covered with a long tube, through which the sun's rays entered normally upon the receiving surface. The solar constant as measured with the two disks was in agreement to less than 1 per cent. It was therefore evident that the radiobalance was giving values which were about 5 per cent below the normal. In this test the ends of the thermojunction wires were about 2.2 mm apart on the disk.

They were then soldered close together in the center of the disks, J_1, J_2, but otherwise the instrument was unchanged. It was then found that the neutral current in J_1 had increased from 1.084 to 1.290 amperes and in J_2 from 1.120 to 1.364 amperes at 25° C. The solar radiation test was repeated (9:25:'11) with the surprising result that the radiobalance gave values, which, although in agreement to less than 1 per cent for the two disks, were 24 to 25 per cent *higher* than the value obtained by the sunshine recorder. In the third trial the thermojunction wires were separated about 1.8 mm and the solar radiation test was repeated on an unusually clear day (10:4:'11), when the air was free from dust. In this trial the radiobalance gave values which were 2.7 per cent higher than were obtained with the sunshine recorder. It is therefore evident that the supposed absolute values as determined with this radiobalance are erroneous and that in the last trial accident alone gave observed value so close to the true one. By trial one could of course place the junctions so that the errors would be negligible.

While it is disappointing to find that this instrument does not give directly the intensity of radiation in absolute value, it is possible to calibrate it against a known standard, just as was done with the sunshine recorder, when it should prove an excellent secondary standard pyrheliometer. The instrument just described is very sensitive, responding quickly to the passage of water vapor which is not visible to the eye. In fact, for low altitudes it follows the variation in atmospheric transmission with greater speed than is desirable. These comparisons are based on data obtained, when at intervals of two to four minutes, there was no fluctuation in the atmospheric transmission and when the thermometer reading was either stationary or was changing slowly. Furthermore, the maximum fluctuations in solar radiation, if they had been measured, could not cause the discrepancy herein recorded. The numerous details as to leakage, etc., were investigated and the only thing that will account for the results is the question of the location of the thermojunction in, and the temperature gradient of, the disk. That there is no exact temperature compensation is shown on testing the neutral current; for on throwing off the current the galvanometer gives a deflection (owing, no doubt, to the heat generated in the wires which conducts to the junctions) which slowly returns to zero. The cooling effect is localized in the junction while the heating effect is along the whole length of the wires. This appears to be the weak point in the instrument. Whether the cup radiobalance gives more nearly the true value in absolute measure is undetermined. The measurements on a standard lamp, made by Callendar using a disk and a cup radiobalance, differ by about 12 per cent (disk = 0.0420 watt per cm ^{2}; cup = 0.0373 watts per cm ^{2}).

This great variation in absolute values is the common record of all the instruments yet described for the absolute measurement of radiation; and, as mentioned in the beginning of this paper, it is purposed to continue this study of various types of absolute instruments and report on the relative merits of the same at some future time.

APPENDIX I.

THE AUXILIARY GALVANOMETER

The illustration of the galvanometer previously described [44] has been corrected and modified. It is drawn to scale in Fig. 15, and needs no further explanation than that given in the previous paper. In the most recent work a strip of chamois skin is placed around the coils, completely inclosing them, except a small space in front of the mirror which is inclosed with a small window of plate glass. This inclosure is more effective in preventing air currents in the small space between the coils. Because of the difficulty in preparing a straight glass rod, the mirror is now placed on the center of the rod between the two groups of magnets, as shown in Fig. 15. To secure complete damping on 2.5 seconds single swing, a short strip of bolometer platinum, 0.0007 mm thick is attached to the glass rod, just below the mirror. Platinum is used because it does not hold an electric charge and, because of its thinness, it weighs very little.

The needle system in present use consists of two groups of tungsten steel magnets from 1.2 to 1.6 mm in length, 0.2 mm in width and 0.1 mm in thickness. They are mounted so that each group of magnets has the form of an ellipse. The mirror is of thin microscope cover glass about 1.5 × 2 mm, platinized by cathode discharge [45] and attached to the suspension with soft wax.

To make the suspension, the individual magnets are mounted upon a glass plate by means of LePage's glue. A little shellac is placed on the glass rod, which is then laid upon the two groups of magnets. After the shellac has dried the system is removed from the glass plate by soaking in water. The groups of magnets are

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[44] This Bulletin, **4**, p. 391, 1909.

[45] For details in making cathode mirrors, see papers by Longden, Phys. Rev., **11**, p. 40, 1900; Leithauser, Zs. Instk., **28**, p. 113, 1908; this Bulletin, **7**, p. 197, 1911.

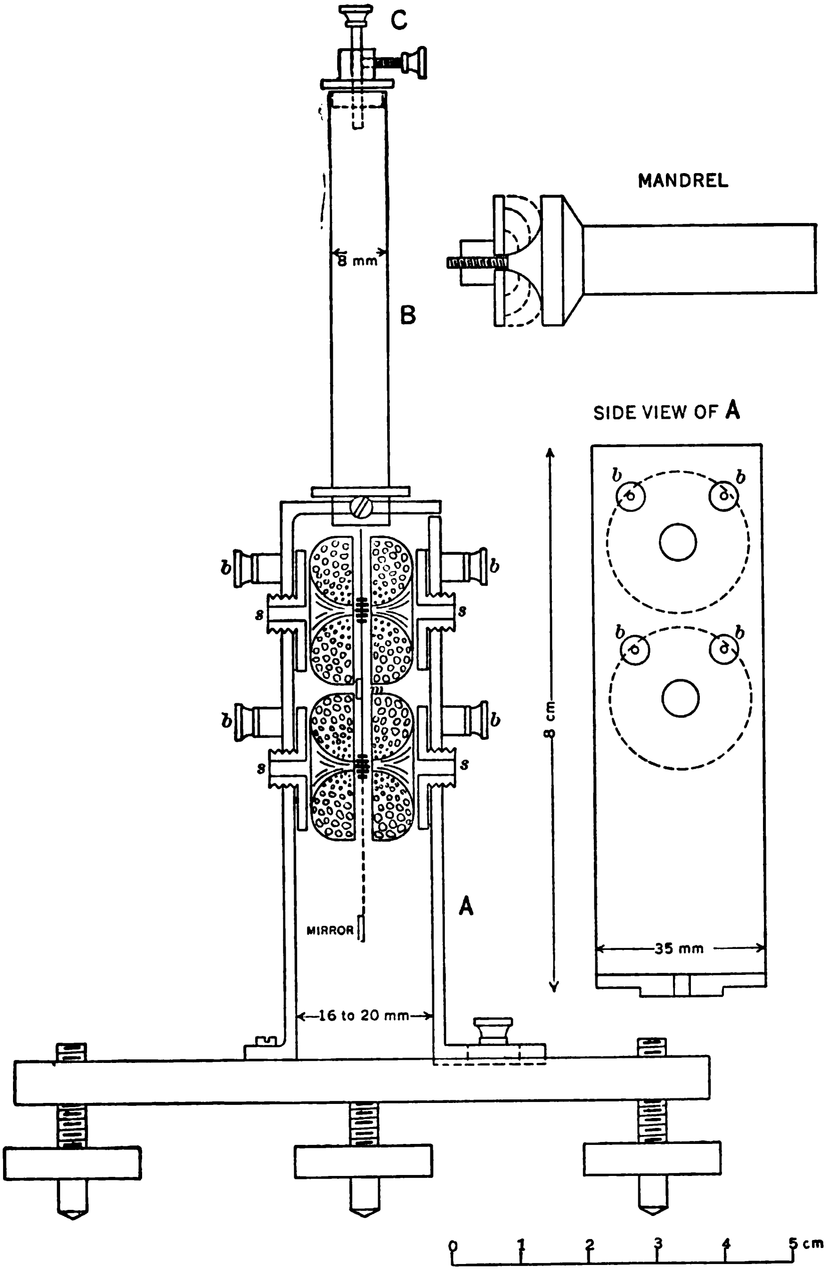
C
MANDREL
8 mm
B
SIDE VIEW OF A
b
s
m
MIRROR
A
8 cm
35 mm
16 to 20 mm
0 1 2 3 4 5 cm

Fig 15

then coated with asphaltum varnish to prevent moisture from being absorbed by the shellac. The magnets could of course be attached to the glass rod by using only the asphalt.

(*a*) **Sensitiveness of Galvanometer.**—In addition to the illustrations given in the previous paper, of the great variation that is possible in the galvanometer sensitivity by making slight changes in the suspension, the experience with a 12-magnet (6 in each group) system may be cited. By removing one magnet from each group, thus making the 10-magnet system shown in Fig. 15, the sensitivity was increased (by decreasing the weight) from 2.4×10^{-10} ampere to 1.4×10^{-10} ampere for the same period of 10 seconds and by adding the light damping vane of platinum (placed between the mirror and the lower group of magnets) this sensitivity remained unchanged.

The sensitivity of the galvanometer changes with the diurnal changes in the earth's field, so that when the humidity (which may affect the shellac on the magnets) is low, it is not an uncommon experience to find the galvanometer sensitivity to vary 10 per cent during the day, and have it return to practically its original value by the following morning. When the humidity is high, the shellac on the magnets warps the system, changing the astaticism sufficiently to mask the effect of the earth's field.

Wooden supports are also subject to warping with changes in humidity, which may shift the large iron shield relative to the galvanometer, thus changing the astaticism. This difficulty has now been overcome by having the galvanometer and its numerous iron shields rest upon one continuous base of marble.

The sensitiveness of the galvanometer (undamped) is approximately proportional to the square of the period. In the present tests the sensitiveness was found to be proportional to the period, owing to the air damping of the light magnet systems, as shown in Fig. 16, which gives the behavior of a 10-magnet system, with a platinum vane. It is just damped on 2.5 seconds single swing, the weight (about 8 mg) being sufficient to avoid the effect of earth tremors.

In the small coil galvanometer, the small mirror limits the use of the scale to a distance of 1.5 to 2 m, depending upon the planeness of the mirror. In the Du Bois and Rubens galvanometer the mirror is large and the high sensitivity of this instrument is obtained by using the scale at a distance of 4.5 to 6 m. Present experience indicates that for prolonged routine work it is better to use mirrors about 2.5 by 3.5 mm area and attempt to gain in sensitivity by placing the scale at 2.5 to 3.5 m instead of having the scale at 1 to 1.5 m, which is the limit for smaller mirrors.

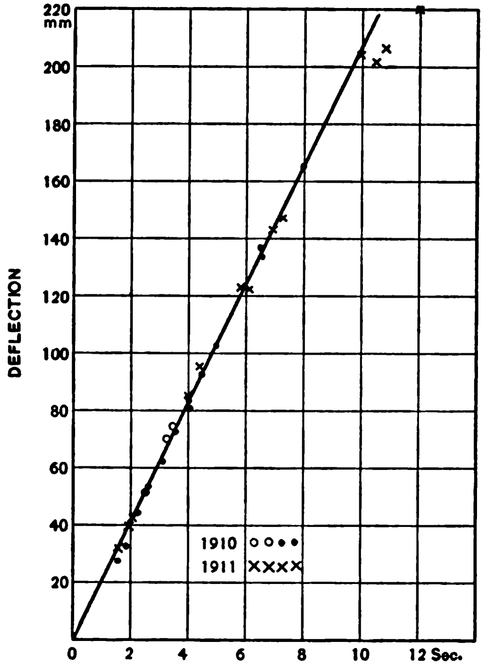

Fig 16

The present galvanometer suspension has not been remagnetized for about two years. During this time the sensitivity has decreased about 30 per cent.

(*b*) **Proportionality of Galvanometer Deflections.**—In the previous paper[46] experiments were described showing the relations between the currents through the galvanometer and the corresponding deflections. For a small coil (18 mm diameter, magnets 1 mm long) the deflections were proportional to the current up to about 7 cm. It was shown that by a judicious selection of longer galvanometer magnets, the proportionality of deflections with current may be made to hold true for large deflections (20 to 30 cm, which is practically the tangent law) with but slight loss in sensitiveness for a given period. This is well illustrated in Fig. 16, which gives the behavior of the 10-magnet system (5 in each group; magnets 1 to 1.6 mm long) provided with damping vanes and used in the present galvanometer having 20 ohm coils (5.09 ohms in parallel; coils 32 mm diameter). Here the proportionality holds to 18 or 20 cm deflection.

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[46] This Bulletin, 4, p. 391, 1908.

(*c*) **Magnet Shielding.**—For shielding a galvanometer magnetically, commercial soft iron pipe about 25 cm in length, and of various diameters, known as "black nipples," may be easily obtained. These shields usually become permanent magnets in handling, and there is great difficulty in lengthening the period of the galvanometer needle. It is therefore a matter of trial in placing the control magnets in such a position that they weaken the combined fields of the shields, and lengthen the period of the galvanometer. In fact, it was found easier to place a short magnet (steel file) under the galvanometer base so that it controls the suspended system and brings the mirror into view of the observing telescope, and then to weaken its field than to overcome the complex field (which, of course, remains but is not dominant) of the shields by means of the control magnets. A sheet of glass rests securely upon the iron shields upon which is placed a magnet (a large iron file) of suitable strength. To weaken the field of the short control magnet, which is placed near or under the galvanometer, this large magnet is rotated about a vertical axis until the galvanometer needle, which is following this rotation, passes through a neutral point, and rotates in the opposite direction. At this point the galvanometer needle will take a long period, provided the control magnets are not too strong.

For magnetically shielding the small coil galvanometer (coils 32 mm diameter) used in the present work, five sections of annealed soft steel pipe, about 30 cm long, inside diameter 7, 10, 15, 22, and 32 cm, respectively, and 4 to 6 mm thick are used. Within these cylinders of soft steel, and resting on the base of this galvanometer, Fig. 15, is a laminated cylinder, about 20 cm high, of the best quality of transformer iron, made by rolling up and riveting 8 turns of iron 0.4 mm in thickness.

The mirror is viewed through slits 1 cm high cut into the shields. Although slits (borings, flaws, etc.) are considered detrimental[47] it appeared to make no appreciable difference in the shielding to use the slits and mirror far below the coils, or to have the slits at the center as now used in viewing the mirror between the coils, as shown in Fig. 15.

An inner shield was made[48] from Swedish iron which had a circular hole, bored vertically to admit the suspended system and the coils, which were mounted in paraffin. This inner magnetic shield was found to be superior to the others just described, since it is easier to anneal and does not become a permanent magnet in handling. The shield with the glass windows serves as a further protection against air currents. It is used with the 20-ohm coils (mentioned in the previous paper) which are 18 mm diameter.

Another inner magnetic shield is shown in Fig. 17, which gives a front and side view. It was made of two bars of Swedish iron, about 2.5 by 5 by 9 cm. The coils are imbedded in the iron as shown in the dotted lines in Fig. 17, by means of soft wax, the lead wires are brought out through glass tubes, t, and secured by brass screws, s, which are insulated in fiber. This is about the simplest mounting and shield that one can make. It is practically air tight, and its massiveness does not allow the coils and the inclosed air to follow sudden temperature variations. The whole should be given a thorough coating of shellac to prevent minute scales of oxide, which are formed on annealing, from becoming attached to the galvanometer needles. The following is an experience of this kind. The 32 mm coils and suspension, Fig. 15, were mounted in this shield. It was found that, starting with a certain period, e. g. four seconds, and the suspension in the zero position, when the suspension was deflected through a certain angle, the period changed and the deflection went off the scale. The exact cause of this could not be learned, but it appeared to be owing to a lack of symmetry of the distribution of the iron in this shield, which makes it less desirable than the preceding form. A somewhat similar experience was encountered with the (fully shielded) galvanometer illustrated in Fig. 17. When deflected to the right the needle began to drift, indicating a change in astaticism and an increasing period. No effect was observed when the suspension was deflected to the left. When examined under a microscope a small speck of iron oxide, about 0.05 by 0.1 mm was found pivoted on the end of one of the small magnets. On removing it the difficulty was remedied. Evidently as the magnet system rotated, thus changing the direction of the magnetic field

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[47] Nichols and Williams: Phys. Rev., 27, p. 250; 1908.

[48] This bulletin, 4, p. 391; 1908.

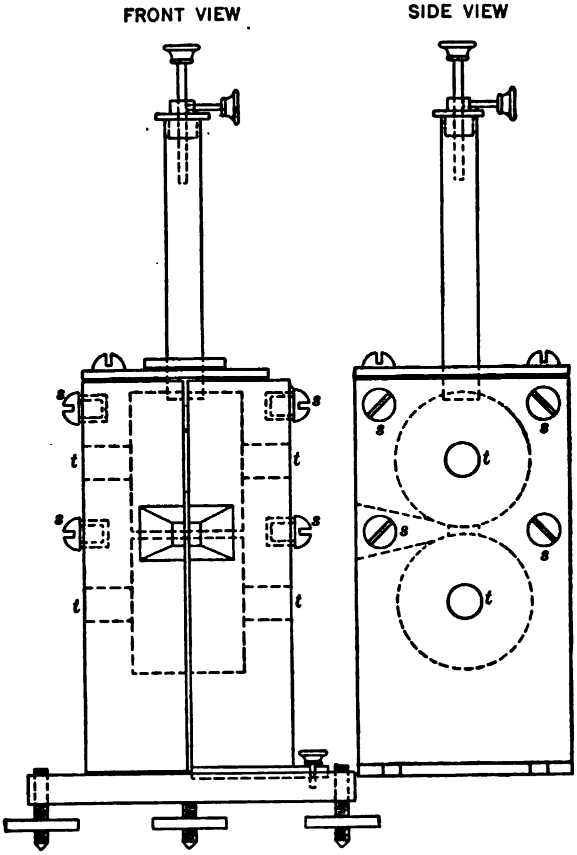

Fig. 17

upon it, relative to that which obtained when in the zero position, the speck of iron oxide was acted upon in a different direction, and, being pivoted on the end, was free to turn, thus changing the astaticism of the suspended system.

It is customary to provide a symmetrical pair of control magnets (30 to 40 cm above the coils) placed upon a contrivance which permits an independent horizontal rotation and a vertical motion.[49] This is desirable in work extending over a long time, for the astaticism of the needle system is constantly changing, which requires a frequent adjustment of the control magnets in order to keep a fairly constant galvanometer period. As already mentioned, after painting the magnets with asphaltum (which is not hydroscopic) or mounting them therein, and after securely mounting the galvanometer and shields upon a suitable base, the writer has had no further difficulty with the change in astaticism. The galvanometer has retained a period of 2.5 to 3 seconds single swing for weeks without adjustment.

WASHINGTON, December 8, 1911.

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[49] See Wiedemann's "Electricitat."

ANTENNA RESISTANCE

By L. W. Austin

A preliminary note on this subject[1] showed that, in accordance with the Hertzian theory, the antenna resistance varies approximately inversely as the square of the wave length up to a point which is slightly less than twice the fundamental wave length of the antenna. Beyond this point the resistance again rises nearly in direct proportion to the wave length. This increase in resistance with wave length is not explained by the theory and is not accompanied by any increase in radiation. It is therefore supposed to be connected in some way with the losses due to the currents in the earth beneath and in the neighborhood of the antenna, although this view—that the earth current resistance increases with wave length—is not supported by independent investigations of earth current resistance.[2]

The peculiar nature of the results obtained in the original investigation, using an artificial antenna, has made it desirable to verify the results by other methods. The circuits employed in the first investigation are shown in Fig. 1. The method, in brief, is the substitution of an air condenser in place of the antenna and ground, keeping the inductance common to both circuits and introducing resistance in the condenser circuit until the current becomes the same as that observed when the antenna and ground were used. In the figure A is the antenna, E the ground, L_1 the tuning inductance, C_1 an air condenser for tuning to very short wave lengths, *Th* a thermoelement, G a galvanometer, and C_2 a variable air condenser set at the capacity of the antenna to be measured. A small inductance L_2 was sometimes inserted in circuit with the condenser C_2 to represent the antenna inductance. This has little influence on the results and at least for the longer wave lengths may be perfectly well omitted. S_1 and S_2 are switches for connecting either the antenna and ground or C_2 to the rest of the circuit. R is a resistance introduced in the circuit C_2 to bring down the thermoelement deflection to the same value as that observed when the antenna and ground are in circuit. The high frequency resistance consists of separate units of fine constantan wire inserted in mercury cups. The measurement circuit is excited by a buzzer-driven wave meter W of the ordinary type.

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[1] J. of Washington Academy, 1, p. 9; 1911.

[2] H. True: Jahrbuch d. drahtlosen Telegraphie, 5, p. 125; 1912.

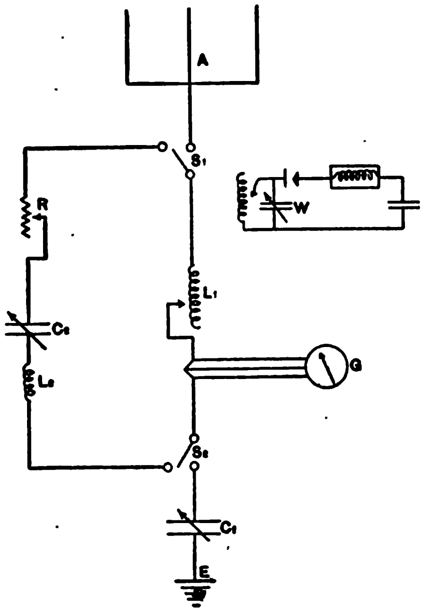

Fig. 1

The second method employed was the well-known decrement method of determining resistance. Here the antenna was excited by a wave meter of known logarithmic decrement provided with a buzzer. The reading of the condenser of the wave meter was noted for maximum deflection of the thermoelement in the antenna and also when the wave meter was thrown out of resonance by an amount sufficient to reduce the antenna thermoelement reading to one-half. The expression for the sum of the decrements is, then,

$$\delta_1 + \delta_2 = \pi \frac{C_m - C}{C_m}$$

where C_m denotes the condenser reading for maximum deflection and C the reading for which the deflection is reduced to one-half. As δ_1, the wave meter decrement, is known, the equation serves to give the value of the antenna decrement δ_2. The resistance of the antenna is obtained from the decrement according to the equation

$$R = 2nL\delta_2.$$

A third method is based on the Bjerknes equation of the current square in the second of two coupled circuits.

$$I^2 = \frac{\text{Constant}}{\delta_1^2\,\delta_2 + \delta_2^2\,\delta_1}. \tag{1}$$

Here I represents the R. M. S. current in a circuit excited inductively by another, δ_1 the decrement of the first circuit, and δ_2 that of the second. If the decrement of the first circuit is very great compared to that of the second, the second term of the denominator may be neglected, and

$$I^2 = \frac{\text{Constant}}{\delta_1^2 \delta_2};$$

that is, doubling the resistance in the second circuit will reduce the current square to one-half. If the antenna is excited by a highly damped circuit, the readings of a galvanometer attached to a thermoelement in the antenna will be reduced to one-half when a resistance equal to the total antenna resistance is inserted in the antenna. In practice it is impossible to obtain an exciting circuit whose decrement is great enough to allow using this method in connection with an antenna unless a correction be made for the second term of the denominator of equation 1.

TABLE I

Correction to be Added to Observed Resistance Required to Reduce I^2 to One-half for Various Ratios of Decrement in Half Deflection Method

$\frac{\delta_1}{\delta_2}$	Correction (per cent)
3	42
4	38
5	28
7	23.5
10	17.5
15	12
20	8.7
30	6.2
50	4.2

Corrections for various ratios of δ_1 to δ_2 are given in Table I. These corrections are to be added to the resistance which reduces the value of I^2 to one-half to obtain the actual antenna resistance. For rough testing in the case of quenched gap sets this correction may be taken as about 20 per cent. This assumes four waves in the primary train.

It is to be observed that in the last two methods the resistances of the inductance of the antenna and of the inserted thermoelement are added to the resistance of the antenna and ground alone as measured by the artificial antenna method. The high frequency resistance of the inductance at short wave lengths may amount to considerable, therefore it is to be expected that these methods will give higher values than the one first used.

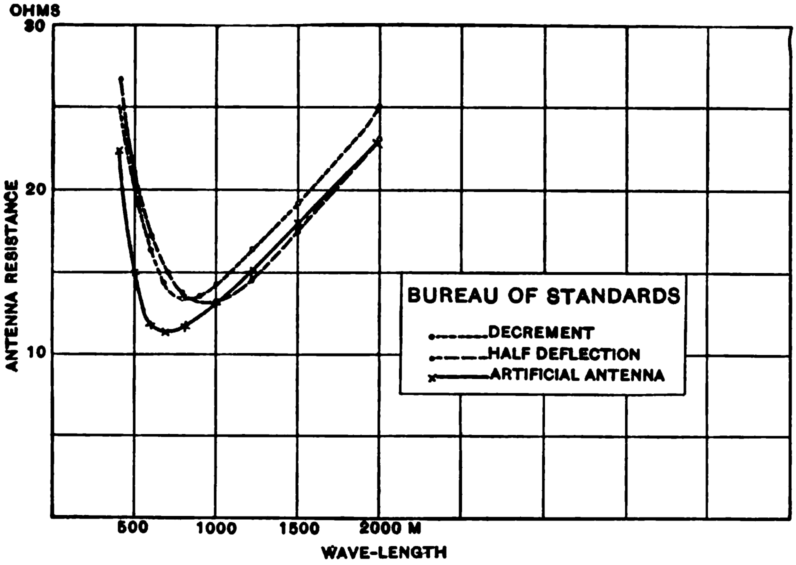

Fig. 2

Measurements by these three methods have been made on the antenna at the Bureau of Standards and the results are shown in Fig. 2. As was to be expected from what has been already said, the artificial antenna method gives in general the lowest values, while the decrement method gives a curve lying above the artificial antenna curve showing a difference of a little more than 1 ohm at the longer wave lengths, and for the shorter wave lengths a still greater difference on account of the increase in the resistance of the antenna inductance with decreasing wave length. The half deflection method gives a curve which follows the decrement curve closely at the shorter wave lengths and the artificial antenna curve at the longer wave lengths. This is undoubtedly due to errors in the determination of the ratio of the decrements in the quenched gap and antenna circuits. These errors are not at all surprising when it is remembered that the decrement of a spark circuit has been shown by experiment to be not by any means logarithmic in its character.[1]

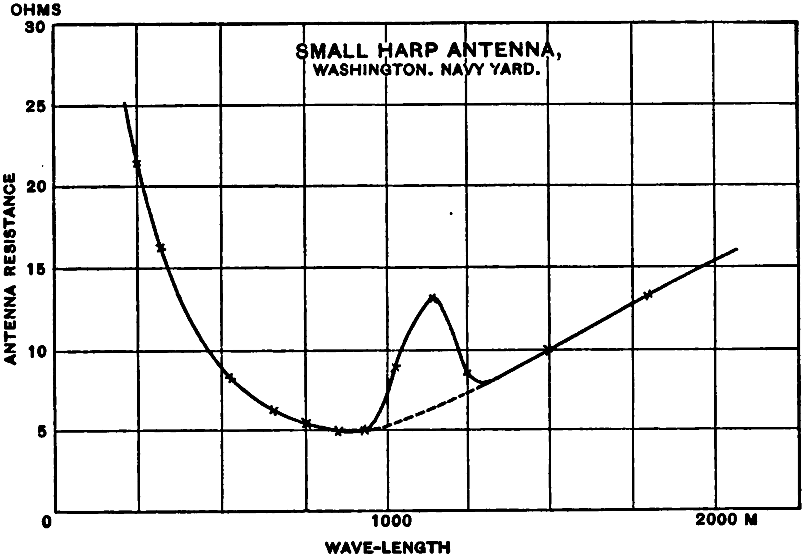

Fig. 3

Of the three methods, that of the artificial antenna is undoubtedly the most accurate, while that of the half deflection is the least so. The latter, however, is by far the simplest for ordinary station testing, as it may be applied without the use of any extra apparatus, the readings being taken with the regular hot wire meter, sufficient suitable high frequency resistance being added to reduce the square of the antenna meter current to one-half.[2]

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[1] J. Zenneck: Ann. der Phys., 18, p. 822; 1904.

[2] For wave lengths above 500 meters it may be assumed without great error that the high frequency resistance of No. 20 (0.81 millimeters) Advance or manganin wire is the same as its direct-current resistance. The resistance must of course be made up noninductively and preferably in a number of separate units. This wire will carry 7 to 8 amperes without heating.

Since the preliminary paper was published, the resistances of a large number of antennas, both at shore stations and on ships of the United States Navy, have been measured by the artificial antenna method. The results of some of these are shown by the curves of Figs. 3 to 7. The curves in general are self-explanatory, indicating that the minimum resistance in a well-installed

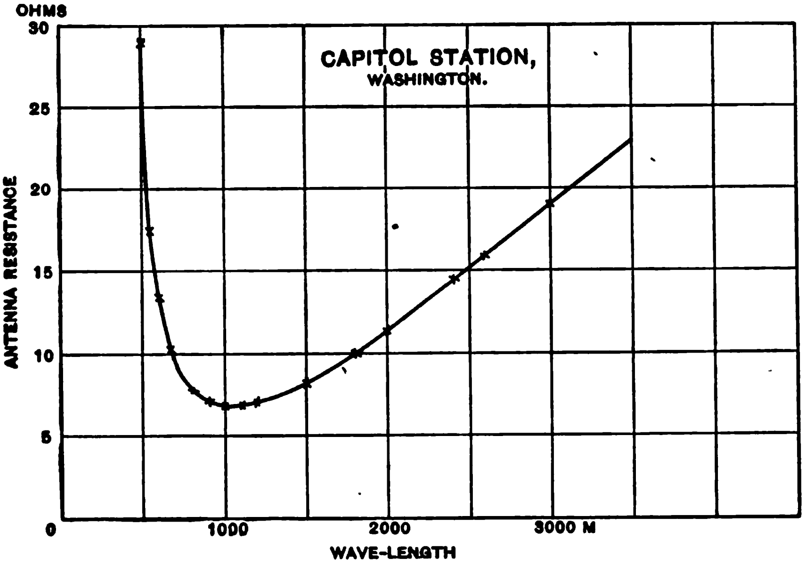

Fig. 4

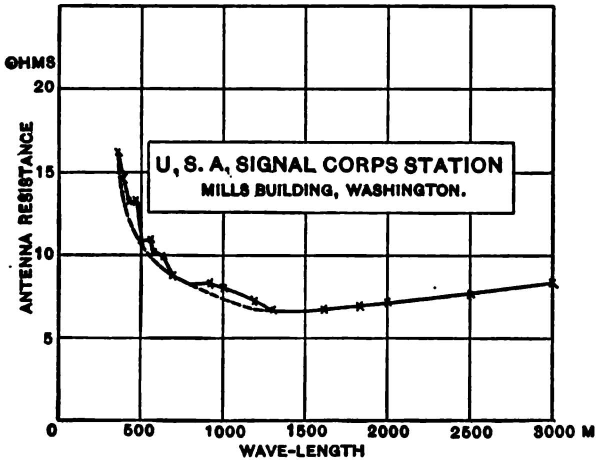

Fig. 5

ship set should not rise much above 2 ohms. It appears to be difficult, if not impossible, to bring the resistance of land stations as low as this. The irregularities in the curve of the Signal Corps antenna installed above the roof of the Mills Building in Washington show clearly the effects of resonance in the metal portions of the building, while the curve for the harp antenna at the Washington Navy Yard shows a large increase in resistance at the point where it is in resonance with the main antenna of the wireless station. These two examples prove the necessity of taking care that no wave length used shall correspond to the period of any metallic structure in the neighborhood of the antenna, such as the steel masts and rigging of ships.

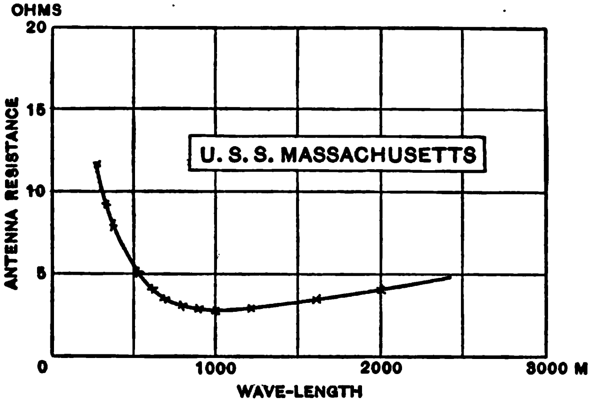

Fig. 6

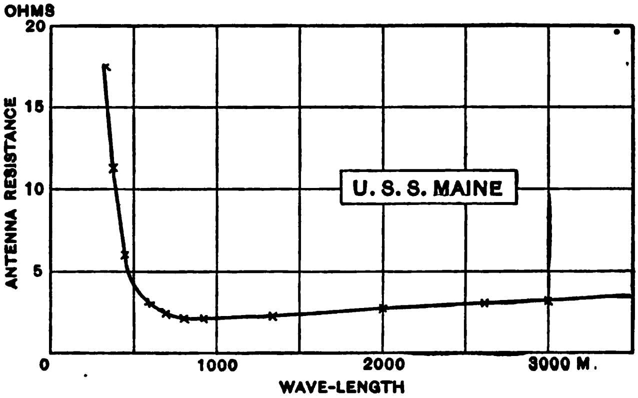

Fig. 7

TABLE II

Stations	Antenna type	Length (meters)	Capacity µf	Height (meters)
Bureau of Standards	Harp	42.6	0.00126	54.8
Signal Corps	Flat top	44.5	.00171	39.6
Capitol	....do	85	.00232	44.2
Washington Navy Yard (small antenna)	Harp	51.8	.00073	54.8
U. S. S. Maine	Flat top	32.9	.00125	38.4
U. S. S. Massachusetts	....do	24.4	.00110	39

The observations for this paper have been taken for the most part by my assistants, Mineratti and Scanlon, chief electricians, United States Navy.

U. S. NAVAL RADIOTELEGRAPHIC LABORATORY,
WASHINGTON, March 1, 1912.

ENERGY LOSSES IN SOME CONDENSERS USED IN HIGH-FREQUENCY CIRCUITS

By L. W. Austin

The following experiments have been carried out for the purpose of determining the energy losses in different types of sending condensers, including compressed air, Leyden jars in air and immersed in oil, paper condensers, and molded condensers (composition dielectric), all used, with the exception of a few experiments, at a maximum voltage of 14 500 volts, this being a voltage which is frequently employed in the newer wireless sets of the United States Navy. In most of the tests the condensers were of approximately 0.006 microfarad capacity and the wave length was about 1000 meters. Current was taken from the city mains at 60 cycles and raised to the necessary voltage by means of an open-core transformer.

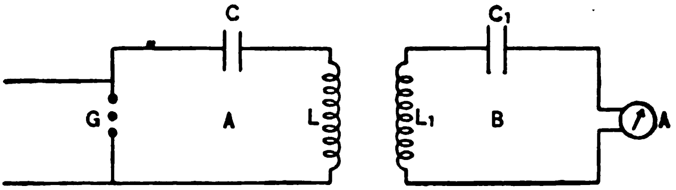

Fig. 1

Two forms of circuit were used in the experiments. The first form, in which an absolute determination of the losses of the compressed-air condenser was made, is shown in Fig. 1. In this circuit A contains a quenched gap G of the Telefunken type, a condenser consisting of seven Leyden jars in air, and an inductance sufficient to produce a wave length of 1000 meters. To this was coupled the testing circuit proper B, which was made up of the condenser under test, an inductance, and a hot-wire ammeter. The inductance was of the flat strip Fessenden type and consisted of a coil of 30 turns, 19 cm in diameter and 8 cm in length, of which about 12 turns were used. The phosphor-bronze strip of which the coil was composed was 0.62 cm wide and 0.13 cm thick, the wide dimension being perpendicular to the axis of the coil. This method of winding gives great compactness with large current-carrying capacity, but has the disadvantage of placing a considerable amount of metal at right angles to the lines of magnetic force, thus tending to produce eddy currents. The hot-wire ammeter was of the 6-ampere General Electric type and was provided in most cases with a shunt, the shunt ratio being determined for the frequency used. The high-frequency resistances were of manganin wire 0.081 cm in diameter inserted in mercury cups. These wires had the same direct current and high-frequency resistance at the frequencies used, as was determined by special experiments. Wave length and decrement measurements were made in the usual way by means of a wave meter with thermo-element and galvanometer.

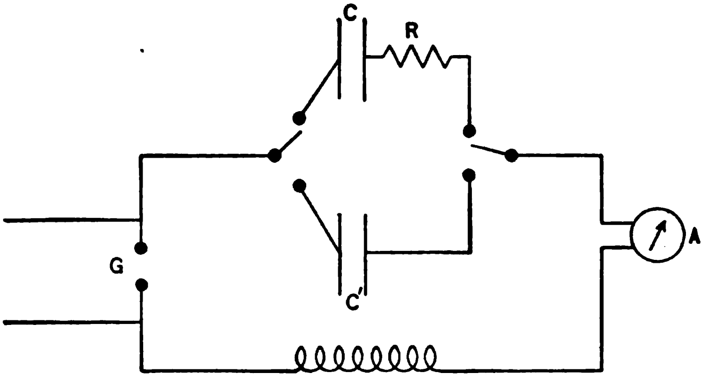

Fig. 2

The second form of circuit is shown in Fig. 2 and is identical with the first form except that the quenched gap circuit is omitted and a parallel cylinder spark gap is introduced into the testing circuit. The spark gap consisted of two parallel cylinders of zinc adjustable for distance and parallelism. In this form of gap the spark runs from point to point insuring good insulation after each discharge without the use of a blower when a moderate amount of power is used. The spark voltage was determined by a parallel micrometer gap.

The Leyden jars furnished for the test were all of them of the copper-coated type. Two types were furnished by the Wireless Specialty Co., type 1 having a somewhat heavier copper coating than type 2. The Moscicki condensers were of their well-known form incased in brass tubes with the glass thickened at the edges of the conducting coatings and with these edges covered by an insulating liquid. The paper condenser was of a well-known make.

LOSSES IN THE COMPRESSED-AIR CONDENSER

The apparatus in this experiment was arranged as shown in Fig. 1, the object being the absolute determination of the resistance of the standard compressed-air condenser already described. The data of the experiment are given in Table I. According to this the resistance of the condenser is 0.14 ohm.[1] It is not certain that this is all a resistance in the condenser proper, but it may consist partly of contact resistance and may be also in part due to eddy current losses, owing to the proximity of the large metal case of the condenser to the rest of the circuit. The amount may quite possibly be in error by 0.05 ohm.

TABLE I

Resistance of Compressed-Air Condenser

[Quenched gap excitation. See Fig. 1]

Capacity	0.00575 mf
Inductance	0.051 mh
Wave length	1020 m
Volts, maximum	14 500
High frequency resistance of—	
Inductance (measured)	0.39 ohm
Leads and ammeter (measured)	0.25 ohm
Decrement of circuit plus wave meter	0.058
Decrement of wave meter	0.032
Decrement of circuit	0.026
Resistance of circuit	0.78 ohm
Resistance of compressed-air condenser	0.14 ohm

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[1] In some other experiments with a different arrangement of apparatus a loss equivalent to as much as 0.25 ohm was observed in the air condenser.

COMPARISON OF CONDENSERS AT CONSTANT VOLTAGE

The arrangement of the apparatus is shown in Fig. 2. The equivalent resistance of the condensers was determined as follows: The current in the main circuit was first measured with a Fessenden compressed-air condenser of 0.00575 microfarad capacity. This being taken as a standard, the current was next determined, using the condensers to be tested, the capacity always being approximately the same as the compressed air. The switch was then shifted so as to throw the compressed-air condenser again into circuit and sufficient manganin resistance wire placed in circuit to reduce the current to the same value as that observed with the condenser being tested, this resistance representing the difference between the compressed air and the condenser under test. In order to take account of the slight variations in current, observations of the ammeter were made every 5 seconds for 50 seconds and the average taken. To give an idea of the degree of steadiness of the current and the accuracy of the observations, the record of one complete set is given in Table II. It was found necessary at the close of each set of readings to clean the gap, as otherwise the readings became less regular and in general the resistance of the gap increased.

TABLE II

Ammeter Readings for Three Wireless Specialty Jars in Air, and Compressed-Air Condenser

[14 500 volts. Wave length 1000 m. Current about 8 amperes]

W. S. (1)	C. A.+0.9 ohm	W. S. (1)	C. A.+0.8 ohm
44	44	44	45
43.5	44.5	44	45
44	43	44	44.5
44	43.5	44.5	44.5
44.5	43.0	44	44
44	43.5	44.5	45
44	43	43.5	44.5
44	43.5	44	45
44	43.5	44	45
43.5	44	44.5	45
43.95	43.55	44.10	44.75

Difference in resistance=0.86 ohms.

TABLE III

Condenser Resistances at Constant Voltage

[Volts = 14 500 (max.) Current = 7–8 amp. Wave-length = 1000 m (about)]

	Units	Capacity (mf)	Resistance (ohms)
Leyden jars in air:			
Wireless specialty (1)	3	0.00603	1.08
Wireless specialty (2)	3	.00605	1.19
Telefunken	3	.00612	1.59
United wireless	2	.00603	1.83
Moscicki (special jar)	1	.00548	0.57
Paper	1	.00580	2.19
Murdock (molded condensers)	3	.00535	0.41
Molded micanite	3	.0041	2.91
Wireless specialty (2) in oil	3	.00605	0.28
Glass plates in oil	2	.0042	0.58
Fessenden compressed air	1	.00575	0.14

Table III contains the comparison of various condensers with the Fessenden compressed-air condenser at 14 500 volts.

In order to determine the actual resistance of the condensers as given in the table it was necessary to add to the resistance difference observed the resistance of the compressed-air condenser and a small correction for the differences in current due to slight differences in capacity. A curve for this purpose was determined experimentally. In the case of the paper, the molded condenser, and the jars and plates in oil, brushing was for the most part prevented by their construction. Their losses, therefore, are in the dielectric. The rather high energy loss of the jars in air is chiefly a brush loss.

COMPARISON OF CONDENSERS AT VARIOUS VOLTAGES

The decrement of the circuit containing the three wireless specialty jars in oil was measured at voltages from 4700 to 18 500 volts, the apparatus being arranged as in Fig. 1. The results are given in Table IV. It is seen that there is no certain change in the decrement between these limits of voltage. Similar experiments were also carried on with glass plates in oil, the compressed-air condenser, and with the Murdock molded condensers with the same result.

TABLE IV

Leyden Jars in Oil at Various Voltages

Volts (maximum)	4700	7100	11 400	14 500	18 500
Decrement	0.0435	0.0440	0.0445	0.0445	0.0445

Next a comparison was made at various voltages between three jars in oil and three jars in air of equal capacity, the circuits of Fig. 1 being used. The method of comparison was the same as that used in Table III. The results are shown in Table V and Fig. 3. The table and figure indicate that the losses of the jars in air increase approximately as the square of the voltage[2] from 10 000 volts where the brushing becomes noticeable up to about 22 000 volts. Above this point the increase becomes more rapid. It was observed that the glass at the edges of the conducting coatings became very hot above this voltage and it seems probable that here the internal losses begin to increase rapidly.

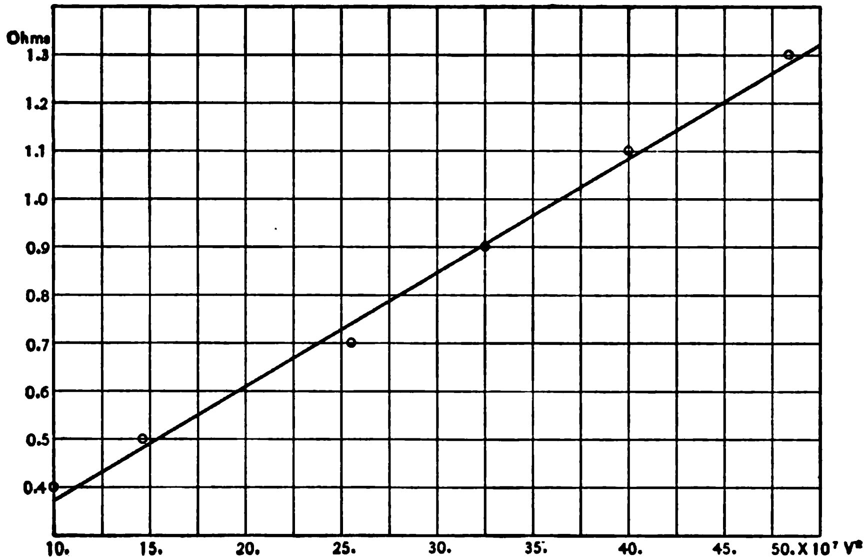

Fig. 3

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[2] Fleming: Proc. Phys. Soc. of London, 23, p. 117; 1911.

TABLE V

Leyden Jars in Air at Various Voltages

Volts (maximum) V	V^2	Resistance (ohms)
10×10^3	10×10^7	0.4
12	14.4	0.5
16	25.6	0.7
18	32.4	0.9
20	40.0	1.1
22	48.4	1.3

From Table V a conclusion may be drawn which is contrary to the ordinarily accepted view; that is, that up to about 20 000 volts the brushing losses are not reduced by placing jars in series if the capacity and voltage remain the same. For if one jar be replaced by four jars in parallel series, the voltage on each jar is reduced to one-half and the loss per jar to one-fourth. The brushing surface is increased four times, therefore the total loss remains the same. An experiment carried out at about 15 000 volts proved that this conclusion was correct.

Another fact which was observed in connection with these experiments is not so easily explained. It was found that the losses in Leyden jars with only their edges immersed in oil are considerably greater than when the whole conducting surface is covered. This result is opposed to the idea that the air losses lie wholly at the edges of the conducting coatings. Observations were also made during the test on losses in jars which had remained for a long time in oil under constant use and also on jars which had been placed in oil and were afterwards used in air without a thorough cleaning. In the first case it was found that when heavy oils were used there was a certain tendency toward carbonization at the edges of the conducting coatings, producing a slight increase in resistance with time. This effect was much more marked when the oil-covered jars were afterwards used in air. When these jars with the carbonized oil at the edges of the plates were replaced in oil the losses continued, often amounting to an equivalent resistance greater than that of clean jars in air. This shows the necessity of keeping the glass around the edges of the conducting plates of condensers thoroughly clean.[3] When condensers are immersed in oil this should be of a noncarbonizing variety.

SUMMARY

Under the conditions of these experiments the following results were obtained:

1. The losses in the compressed air condenser used amount, at a pressure of 15 atmospheres, to an equivalent resistance of between 0.1 and 0.2 ohms.

2. Condensers in which brushing is prevented by the nature of their construction show no change in resistance between the limits of observation, 4000 to 20 000 volts, indicating that the internal losses are independent of voltage.

3. Leyden jars of commercial types immersed wholly in oil show losses but slightly greater than those of the compressed-air condenser.

4. The paper and micanite condensers measured show very much larger losses.

5. The resistances of the different Leyden jars in air vary between 1 and 1.8 ohms at 14 500 volts. Between 10 000 and 20 000 volts the equivalent resistance increases approximately in proportion to the square of the voltage.

6. Placing Leyden jars in parallel series, the capacity remaining the same, does not diminish their brushing losses below 20 000 volts.

7. Immersing only the edges of the conducting coatings of Leyden jars in oil gives an equivalent resistance midway between that observed when wholly in air or wholly in oil.

8. Brushing losses are much increased by any semiconducting material on the surface of the glass at the edges of the conducting coatings of Leyden jars.

I wish to express my obligations to my assistants, Minerratti and Evans, chief electricians of the United States Navy.

U. S. NAVAL RADIOTELEGRAPHIC LABORATORY,
WASHINGTON, March 1, 1912.

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[3] The great difference in brushing losses observed in different specimens of glasses is perhaps due to the differences in their hygroscopic character.

SELECTIVE RADIATION FROM VARIOUS SUBSTANCES, IV

By W. W. Coblentz

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I. RADIATION CONSTANTS OF PLATINUM

In a previous paper[1] the most important so-called constant, α, of spectral radiation of various metals was investigated, on the assumption that the spectral energy distribution followed a law similar to that of a perfect radiator, but with different constants. It was found that the supposed constant, α, had a temperature coefficient; and the investigation was continued.

In a subsequent paper[2] the problem was undertaken from the standpoint of the spectral reflecting power of various metals; and an explanation was given of the cause of the variability of α with temperature. This explanation is based upon the fact that if the reflecting power (and hence the absorptivity) were uniform throughout the whole spectrum, the emission would be that of a "gray body." Hence the position of the maximum emission, λ_{max}, should shift uniformly with rise in temperature toward the shorter wave lengths, and the intensity of the maximum emission should increase according to the equation, $E_{max} = BT^{a}$. But the reflecting power of metals has a temperature coefficient[3] which is quite marked in the infra-red, beyond 30μ, and which decreases to a negligible quantity at 3μ to 4μ. Furthermore the reflecting power of metals is low in the visible spectrum and increases rapidly to a fairly constant value beyond 3μ. For the temperatures at which the investigation was made the maximum emission, E_{max}, shifted from the region of 2.5μ to 3.5μ, where the reflecting power is uniform and the temperature coefficient of reflection is negligible, to the region of 1.2 to 1.5μ where the reflecting power decreases (absorptivity and hence emissivity increases) very rapidly with wave length. Consequently, at low temperatures, when λ_{max} is in the region of 2.5 to 3.5μ, the E_{max} should increase as required by Wien's equation ($E_{max}=BT^5$); but at high temperatures, with the λ_{max} in the region of 1.2μ, the E_{max} will have increased by BT^5 plus the increment resulting from the decrease (i. e. increase in emissivity) in spectral reflecting power. In other words, the value of E_{max} is larger than it would be if the reflecting power at 1.2μ were the same as at 3μ, and consequently the value of α varies (decreases) with rise in temperature.

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[1] This Bulletin, **5**, p. 339; 1909.

[2] This Bulletin, **7**, p. 197; 1910.

[3] Hagen and Rubens, Phys. Zs., **11**, p. 139; 1910.

In renewing the investigation there was therefore no expectation of determining a radiation constant, α; but it was purposed to determine a series of spectral energy curves as accurately as possible, and to determine, if possible, one or more temperature coefficients, which applied to the constants of the Wien equation would cause the theoretical curve to fit the observed energy curve at both low and high temperatures.

In order to determine the temperature of the radiating metal (platinum, tungsten, etc.) it was the intention to use a long tube of elliptical cross section and to sight into the interior by means of an optical pyrometer somewhat after the methods carried out by Waidner and Burgess.[4] It was difficult to attain a high temperature because on heavy currents the electrical stresses caused the tubes to collapse. In the meantime, Mendenhall[5] published results indicating that the temperature determined by sighting an optical pyrometer into a V-shaped fold in a strip of metal is closely the true temperature of the metal. This procedure is much simpler than the use of a long hollow tube, and it was deemed sufficiently accurate, for the problem in hand, to measure the temperatures by sighting an optical pyrometer into the V-shaped space which was given an aperture of a little less than 10°. At high temperatures, the electrical stresses decreased the opening still further; and on account of this difficulty it was not possible to operate strips that were more than 3 cm in length on a current of more than 30 amperes. The radiating strip of metal was 4 mm wide; formed by folding a strip 8 mm wide and 0.02 mm in thickness. It was held securely and vertically between two heavy brass terminals. To the lower terminal, which was movable to take up the expansion, a small weight was usually attached to keep the strip taut. No radiation other than that from the central portion of the strip, 1 to 1.5 cm in length, could fall upon the prism face.

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[4] Waidner and Burgess: This Bulletin, **3**, p. 163; 1907.

[5] Mendenhall: Astrophys. J., **33**, p. 91; 1911.

The spectral energy curves were determined by means of a vacuum bolometer,[6] mirror spectrometer, and a fluorite prism. The bolometer strip was 0.6 mm wide and subtended an angle of 4′.

Three series of spectral energy curves were obtained in which the temperatures were measured with an optical pyrometer. In the first series, I to X, inclusive, the length of the platinum strip, between the terminals, was 4.8 cm and the temperature varied from 1004° to 1442° C. In the second series, XI to XV, inclusive, the length of the strip was 2.7 cm and the temperature varied from 1353° to 1691°. This series gave higher values of the constant product $\lambda_{max}T$ than the third series, XVI to XVIII, inclusive, in which the length of the strip was 2.8 cm and in which the temperatures were all lower, varying from 1056° to 1337°. This indicates that the value of the "constant" was affected only by the surface condition (i. e., not the length) of the platinum strip—which becomes rough at high temperatures—and not by the radiation from the cooler ends, for it is to be understood that the temperature of the short radiators is uniform over only about 10 to 15 mm of the central part of the strip. The strips attained their maximum temperature in a few minutes and were easily maintained at a given temperature by means of an ammeter in series with the storage battery. Owing to the thinness of the metal, air currents caused the temperature of the strip to fluctuate several degrees, so that, although a higher accuracy was attainable with the pyrometer, the errors in measuring the temperatures were estimated at 3° to 5° at low temperatures and 8° to 10° at high temperatures. These errors are of course dependent upon the width of the opening of the V-shaped aperture, which had a tendency to decrease at high temperatures, thus affecting slightly the "blackness" of the radiation and especially the accuracy in matching the filament of the pyrometer upon the smaller V-shaped opening in the platinum strip. It will be noticed presently that other difficulties enter into the work which are of greater importance than those involved in the temperature measurements.

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[6] This Bulletin, 7, p. 197; 1910; 9, p. 7; 1912.

Because of the defects in this method of using the platinum strip, and hence of temperature measurement, a series of 12 energy curves was obtained, in which the temperatures were measured by means of a potentiometer and a Heraeus thermocouple, of wires 0.1 mm in diameter. The thermocouple was surrounded with a sheet of mica 0.04 mm in thickness, and no leakage could be detected at high temperatures which ranged from 746° to 1509° C. To preclude any error due to the cooling effect on the junction by thermal conduction along the wires, the thermocouple was folded back and forth several times in order to heat a considerable length of the wires. The same kind of platinum was used as in the preceding method. The strip, 3.5 cm in length, was mounted in the V-shaped form previously used. After inserting the thermocouple, the strip was pressed flat and its edges united. Thus all the operations were the same as before, excepting that the temperatures were measured with a thermocouple instead of an optical pyrometer.

In this series the greater heat capacity of the radiator and the smaller exposed surface reduced the temperature fluctuations caused by air currents; but a new difficulty arose in that the temperature of the radiator did not remain constant when the heating current was constant. This was most marked at high temperatures when evaporation of the platinum became more rapid. As in the preceding series in which the temperatures were measured with an optical pyrometer, the "radiation constants" were found to depend on the temperature. The variation in the value of $\lambda_{max}T$ with temperature is more uniform than in the preceding series owing to the increased accuracy in measuring the relative temperatures, as may be noticed in Fig. 3.

TABLE I

Energy Distribution of Platinum—Temperature Determinations With a Holborn & Kurlbaum Pyrometer

Spectrometer circle	λ	Correction divisors		Energy distribution, corrected and reduced to normal spectrum									
		s. w. × R^3	$(1-r_1)^3$ $(1-r_2)^4$	V 880° C	XVI 1056° C	XVII 1174° C	VII 1216° C	VIII 1271° C	XIII 1353° C	IX 1442° C	XI 1481° C	XII 1625° C	XV 1691° C
° ′													
5 00	0.589μ	0.0284	0.8067	....	....	....	....	....	....	43.30	37.38	126.0	162.4
4 57	.646	.0375	.8073	....	....	....	....	....	....	118.4	94.80	257.1	295.0
55	.698	.0473	.8081	....	....	....	31.51	36.42	34.92	187.9	154.6	348.9	461.9
53	.757	.0630	.8087	....	....	16.49	55.73	55.02	65.60	293.6	237.3	549.5	724.7
51	.836	.0820	.8094	....	11.52	31.19	101.3	105.0	107.8	501.1	382.4	830.3	1064
49	.934	.1033	.8100	6.58	26.79	56.85	200.1	212.6	201.6	772.1	581.9	1176	1436
47	1.054	.1273	.8106	10.08	52.46	101.7	319.5	339.9	314.0	1141	859.2	1639	1815
45	.197	.1498	.8112	29.01	85.60	167.2	459.1	494.1	425.0	1395	1073	1840	2096
43	.357	.1631	.8118	45.40	126.7	234.8	603.1	615.6	514.2	1544	1217	1929	2225
41	.526	.1710	.8124	67.48	166.4	275.2	680.4	692.1	569.8	1560	1225	1901	2140
39	.698	.1710	.8128	88.94	176.9	289.2	676.1	682.0	567.6	1409	1143	1728	1885
37	.868	.1665	.8132	98.39	188.5	287.0	646.0	658.3	528.1	1302	1047	1528	1675
35	2.033	.1600	.8137	106.5	187.8	276.9	617.7	614.1	492.3	1135	932.4	1238	1442
33	.190	.1515	.8141	107.1	176.2	253.9	548.3	559.9	441.5	1014	830.3	1156	1279
30	.410	.1414	.8148	103.5	158.5	225.4	462.0	469.1	380.2	835.8	699.8	869.0	1015
28	.546	.1332	.8154	92.08	141.1	197.4	399.7	408.1	350.0	712.2	624.0	811.4	841.7
24	.801	.1227	.8164	77.87	115.1	152.5	321.7	313.0	251.2	538.6	444.8	599.5	640.5
22	.921	.1183	.8169	73.39	103.4	139.4	284.2	279.3	224.2	464.3	394.0	530.5	563.0
20	3.037	.1140	.8175	70.73	94.76	123.1	252.0	255.4	206.9	426.6	364.0	460.0	497.3
18	.150	.1109	.8181	64.80	84.61	115.9	232.1	235.9	191.0	384.5	318.8	432.5	445.6
14	.367	.1045	.8193	60.40	77.10	99.78	211.6	202.3	158.3	328.1	270.8	358.0	362.8
10	.569	.0980	.8205	52.10	70.93	89.82	178.0	174.7	137.7	283.5	238.5	292.9	315.0
6	.760	.0930	.8216	49.62	64.54	75.19	149.6	155.6	120.0	252.2	206.0	265.0	273.2
4 00	4.031	.0873	.8234	45.10	50.80	67.03	121.2	125.7	103.6	198.5	168.8	225.1	217.2
3 50	.446	.0785	.8263	35.91	40.09	47.78	96.99	96.80	74.86	147.2	123.8	152.0	158.7
45	.638	.0750	.8278	31.50	35.78	42.84	84.12	85.05	65.90	129.3	105.0	140.0	140.8
40	.827	.0716	.8293	28.99	29.50	38.06	74.64	72.13	55.93	111.4	92.60	125.3	114.2
35	5.001	.0687	.8307	25.70	28.30	34.00	62.53	64.46	50.40	101.1	80.22	105.0	107.4
30	.168	.0663	.8321	22.10	25.20	30.63	56.00	57.26	46.92	88.60	75.79	90.61	98.79
20	.486	.0623	.8349	18.28	....	26.52	40.39	48.46	36.32	75.35	61.34	69.20	78.81
2 54	6.240	.0542	.8419	....	....	....	27.61	30.59	25.12	41.72	35.81	38.66	44.92
30	.852	.0487	.8481	....	....	....	....	....	....	....	22.50	25.64	29.28
2 00	7.546	.0433	.8520	....	....	....	....	....	....	....	....	....	....

TABLE II

Energy Distribution of Platinum—Temperature Determinations With a Le Chatelier Thermocouple

Spectrometer circle		Correction divisors		λ	Energy distribution, corrected and reduced to normal spectrum									
		$s.w.\times R^3$	$\frac{(1-r_1)^2}{(1-r_2)^4}$		5 855° C	2 976° C	7 1068° C	6 1119° C	3 1152° C	10 1210° C	8 1227° C	9 1327° C	11 1445° C	12 1509° C
°	′													
5	00	0.0284	0.8067	0.589μ	....	....	....	....	....	....	....	10.48	....	30.11
4	57	.0375	.8073	.646	....	....	....	....	....	....	9.58	23.46	44.28	66.30
	55	.0473	.8081	.698	....	....	....	5.49	9.08	13.08	16.10	39.75	68.79	111.6
	53	.0630	.8087	.757	....	5.69	10.80	13.14	23.95	32.80	32.00	70.21	116.2	192.1
	51	.0820	.8094	.836	....	8.75	19.14	31.06	47.17	53.20	65.84	132.9	200.3	284.9
	49	.1033	.8100	.934	4.67	18.89	32.99	60.00	86.76	96.64	113.2	215.0	308.0	426.0
	47	.1273	.8106	1.054	11.25	44.20	72.19	115.8	161.0	179.9	209.7	368.0	476.0	650.1
	45	.1498	.8112	.197	24.70	81.04	128.6	190.5	263.0	280.1	316.5	524.8	649.9	870.0
	43	.1631	.8118	.357	46.24	135.3	185.6	275.0	369.2	378.0	446.7	673.7	781.9	987.7
	41	.1710	.8124	.526	65.24	176.8	246.6	340.6	431.0	443.9	502.5	730.5	815.8	1013.0
	39	.1710	.8128	.698	85.00	205.5	271.0	360.1	457.1	465.7	510.0	735.1	786.6	969.8
	37	.1665	.8132	.868	97.20	216.9	279.6	368.7	463.1	451.0	508.0	694.4	708.6	880.0
	35	.1600	.8137	2.033	103.5	221.7	270.0	355.0	433.9	432.2	466.1	642.6	663.5	789.4
	33	.1515	.8141	.190	106.4	214.4	259.0	335.0	407.0	399.4	435.0	572.4	581.3	702.9
	30	.1414	.8148	.410	100.2	194.0	234.9	297.6	362.3	341.6	377.1	500.3	488.1	591.0
	28	.1332	.8154	.546	95.13	182.8	221.0	271.1	324.6	317.0	346.4	439.7	434.1	516.0
	24	.1227	.8164	.801	80.93	147.9	170.9	213.6	253.0	242.5	262.9	330.8	320.0	371.8
	22	.1183	.8169	.921	72.81	131.8	154.0	186.0	219.6	211.7	231.3	288.0	252.2	342.0
	20	.1140	.8175	3.037	69.00	123.1	142.4	176.0	204.7	196.5	215.0	266.3	260.0	292.4
	18	.1109	.8181	.150	65.25	112.6	131.2	162.0	187.7	188.2	198.0	249.0	235.4	274.9
	14	.1045	.8193	.367	58.40	101.5	113.7	138.2	160.4	156.8	167.5	206.0	195.0	228.0
	10	.0980	.8205	.569	53.96	91.11	102.0	123.7	140.8	138.6	148.0	178.3	168.0	196.2
	6	.0930	.8216	.760	49.61	81.42	89.19	112.8	126.0	122.0	130.0	155.9	149.5	173.0
4	00	.0873	.8234	4.031	41.19	68.06	76.80	92.39	101.6	101.4	105.5	129.5	120.6	135.6
3	50	.0785	.8263	.446	34.52	54.24	56.26	66.59	77.82	78.19	78.00	95.59	87.67	100.8
	45	.0750	.8278	.638	30.65	47.69	51.06	60.90	65.23	69.25	70.76	80.58	74.79	89.40
	40	.0716	.8293	.827	27.97	41.78	46.82	54.40	59.45	59.30	63.19	73.94	66.70	80.85
	35	.0687	.8307	5.001	24.70	39.08	40.12	50.27	55.20	53.80	54.63	65.40	60.00	70.40
	30	.0663	.8321	.168	22.30	34.79	36.99	44.76	47.20	48.93	48.40	59.07	53.82	61.80
	20	.0623	.8349	.486	18.66	27.16	29.79	37.29	37.40	39.00	40.71	47.83	44.00	51.60
2	54	.0542	.8419	6.240	12.71	16.89	19.06	....	21.04	23.69	24.11	30.70	27.62	29.81
	30	.0487	.8481	.852	....	....	....	....	15.96	....	....	17.67	....	19.35
2	00	.0433	.8520	7.546	....	....	....	....	8.10	....	....	....	....	....

A number of the best curves reduced to the normal spectrum are given in Table I and Table II. The correction factors for reduction to the normal curve are also given. These factors include the variation in dispersion (the slit width, "s. w."); the variation in reflecting power (R; R^3 for three mirrors); the variation in reflecting power with angle of incidence upon the prism face (r_1; r_1^2 for two faces); and the loss by reflection at normal incidence from the fluorite bolometer window and the fluorite prism (r_2; r_2^4 for four surfaces). The last two corrections are computed by means of the well-known Fresnel equations, from the refractive indices and the angle of incidence of the energy upon the prism face.

The radiation sensitivity of the bolometer was easily kept constant while observing a given spectral energy curve; but no attempt was made to obtain all the energy curves at the same sensitivity. Hence the relation between curves obtained on different days is not known. Furthermore, it is not required in the computations herein employed. The computations of the constants are based upon the assumption that the mathematical equation of the spectral energy curve is similar to the Wien equation;

$$E = C_1 \lambda^{-\alpha} e^{-C_2/\lambda T}$$

from which it follows that

$$\lambda_{max} T = \text{Const}; \qquad \frac{E}{E_{max}} = \left\{ \frac{\lambda_{max}}{\lambda} e^{\frac{\lambda - \lambda_{max}}{\lambda}} \right\}^{\alpha}$$

The computations of λ_{max} and of α are obtained from equations (4) and (5) of the previous paper[7] and need not be repeated here. It was there shown that there are no real "constants"; in other words, that the equation expressing the spectral energy distribution is more complex than the one assumed in the computations.

In the previous observations the platinum strip was in an evacuated glass bulb. The operating temperatures were not so high, and the platinum strip retained its original high polish. The values of α decreased from 8 to 6.2 for a change in λ_{max} from 2.2μ to 1.9μ, while in the present work, in air with the platinum surfaces deteriorating (which is supposed to "blacken" the radiation. This would decrease the value of α at any given temperature; but this does not appear to affect the temperature coefficient of α, as may be noticed by the order in which the energy curves were observed—see Fig. 3; XV and XVIII), the values decreased from 6.6 to 6.0 for the same change in λ_{max}, i. e., in temperature. There are several reasons for this difference, the principal one being the highly polished surface of the strip previously used, which would increase the value of α. In Fig. 1 (temperatures by means of optical pyrometer, *A*; thermocouple, *B*) are shown graphically

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[7] This Bulletin, 5, pp. 351 and 352; 1909.

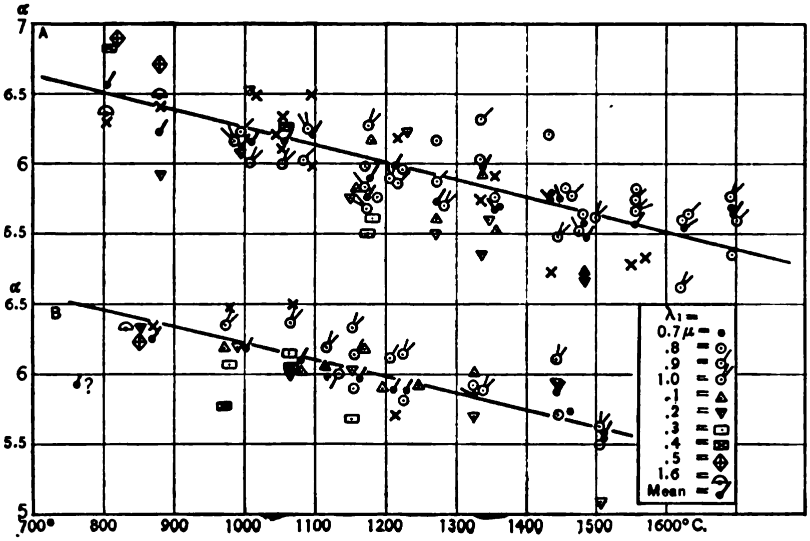

Fig. 1

the results of the computations of α for various temperatures, and for various values of λ_1 taken from the same spectral energy curve; also the mean value, δ, of all the computations of α, of which only a few of the individual values are shown at each temperature. The variations from the mean are rather large, and occasionally even the mean value lies far from the curve, e. g., Fig. 1–*B*, at 750° for α and Fig. 3–*A* for $\lambda_{max}T$, but in both cases the spectral energy curves were poor, and hence should perhaps not have been computed at all. Both series *A* and *B*, Fig. 1, show that in the temperature range of 1100° to 1400° the value of α is of the order of

5.8 to 6.0. It is difficult to determine how much of this variation in α is owing to roughening of the surface (which is supposed to "blacken", i. e., change the quality of, the emissivity) and how much is the result of the temperature coefficient of emission, which, however, is small in this region of the spectrum. As already mentioned the variation in α is probably affected to the greatest extent by the shift of the maximum emission into the region of the spectrum where the reflecting power decreases rapidly with wave length.

The value of λ_{max} is given in Fig. 2 for the optical pyrometer temperatures and energy curves (I to XVIII) and the thermocouple (1 to 12) temperatures and energy curves. In this curve the ordinates are the computed values of λ_{max} which result from taking different values of λ_1 (and λ_2) as explained in the previous paper.[1] All of these curves show a minimum which shifts toward the shorter wave lengths with rise in temperature.

If we take a "black body" spectral energy curve (at 1500° C) and multiply its ordinates (= emissivity) by the absorbing power (100 − Reflection) of platinum, then, from the resulting curve, compute the value of λ_{max} for different values of λ_1 (and λ_2) we obtain the heavy curve shown in Fig. 2, Pt. This likewise has a minimum, which would be still more marked if we had assumed a temperature coefficient of emission for the values of λ_2 in the region of 4μ to 7μ as observed by experiment.

This minimum in λ_{max}, which usually lies in the region of 3.0μ to 3.2μ, is not in the region of atmospheric absorption bands (at 2.7μ to 3.0μ) and it is not to be found in the spectral energy curves of a uniformly heated inclosure, or so-called "black body." The explanation offered for its occurrence is based upon the high temperature coefficient of emission in the region of 4μ to 7μ and the rapid change in emissivity which must follow a shifting of the maximum of the spectral energy distribution into the region of 1.5μ to 1.2μ, where the reflecting power of platinum undergoes a rapid decrease with wave length. In the region of 3.0μ to 3.5μ there is no marked temperature coefficient of emission, and the reflecting power is fairly uniform. Hence in this region of the spectrum there is no marked change in the emission with rise in temperature, other than that which would result if platinum were

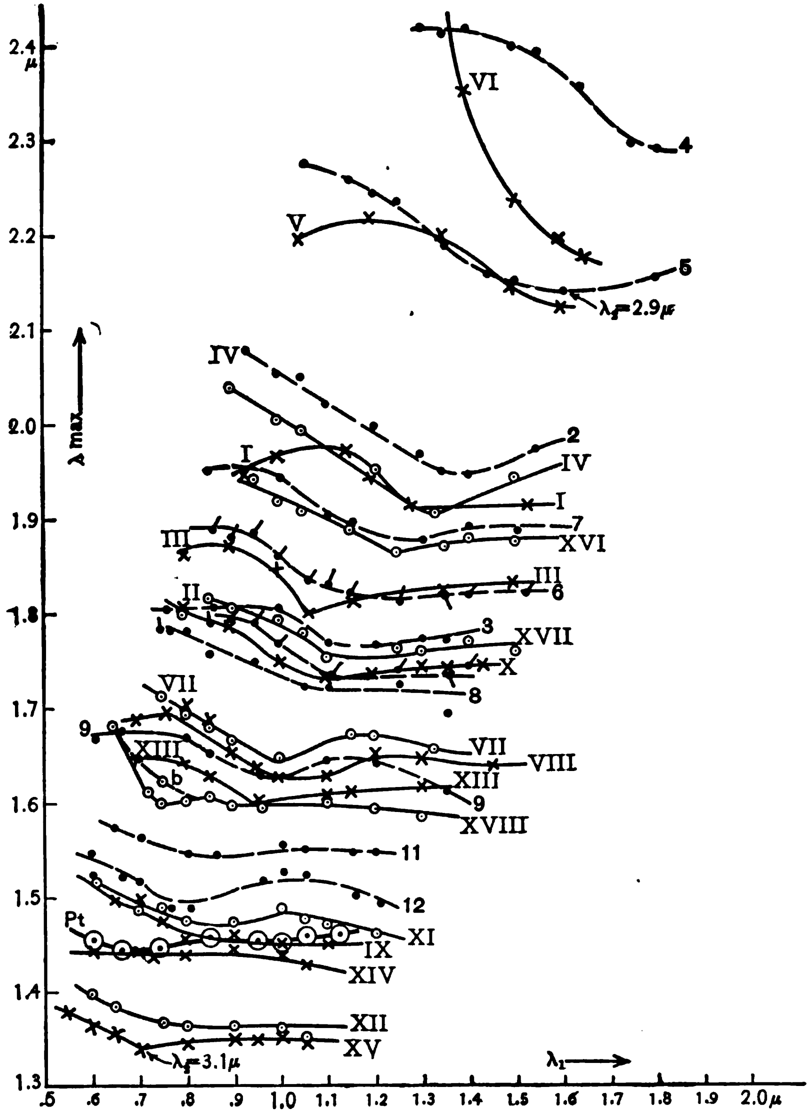
2.4 μ
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
λ max
.5
.6
.7
.8
.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0μ
λ1
VI
4
V
5
λ2=2.9μ
IV
2
IV
I
I
7
XVI
III
III
6
II
3
XVII
X
8
VII
9
XIII
b
VII
VIII
XIII
9
XVIII
11
12
Pt
XI
IX
XIV
XII
XV
λ2=3.1μ

Fig. 2

a "gray body." The emissivity should therefore be a minimum in this region, and when computing λ_{max} from a value of λ_1 in which the corresponding value of λ_2 falls in the region of 3.2μ there follows a low value of λ_{max}. For the same reason, the values of α are very irregular when computed for various values of λ_2. It is, of course, to be understood that the low value of λ_{max} for values of λ_2 in the region of 3μ is owing partly to atmospheric absorption bands at 2.7μ. The observed energy curves are more or less distorted, depending upon the temperature; and to a more marked degree than seems possible as the result of experimental errors. Whether this is the true explanation remains to be determined.

The various values of $\lambda_{max}T$ are given in Fig. 3 for the optical pyrometer temperatures *A* and the thermocouple temperatures *B*. In each series the mean values (⊙ ⊙ ⊙) of all the computations (from 4 to 8 on each curve) of λ_{max} and also the aforesaid minimum values (. . .) are given. The value of $\lambda_{max}T$ increases gradually from 2400 (mean value) at 700° to 2620 (2690 for thermocouple) at 1500° C. These values are independent of the order in which the energy curves were determined, showing that the change in the quality (the "blackening") of the radiation is a true temperature effect and not one resulting from the roughening of the surface with evaporation. To the writer the latter explanation seems far-fetched, because the optical constants of each particle of the roughened surface are the same as before (viz, that of platinum), and the roughening is not of sufficient depth to produce a cavity within which the radiation can become "blackened" by internal reflection.

In the lower part of Fig. 3 are shown the different values of $\lambda_{max}T$ as observed by Paschen.[8] They increase in a line parallel with those herein described. Paschen did not, however, consider this a real variation. The numerical values are 4 per cent lower, owing probably to a difference (50°) in the temperature scale, and especially to a difference (0.09μ) in the dispersion curve of fluorite. An examination of his "Table XIV" shows that the values of λ_{max} pass through a minimum in the same manner as found in the present work, Fig. 2.

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[8] Paschen: Ann. d. Phys. (3), 60, p. 696; 1896.

The theoretical curves for platinum computed on the basis of Wien's equation, using $\alpha = 6$ at 1100° C and $\alpha = 5.6$ at 1500° C, agree fairly well with the observed curves in both cases, being too high in the region of 3μ, intersecting them in the region of 4.5μ, and hence falling below the observed curves in the region of 5μ to 6μ.

The spectral energy curves obtained by the two methods of operation are given equal weight; for in the optical pyrometer series (e. g., energy curve *X*) the temperature sometimes changed or the platinum strip collapsed, while in the thermocouple series the temperature changed as already explained. The errors in the work are not to such a great extent owing to the difficulty in making the temperature measurements as in heating the platinum strip. The values of $\lambda_{max}T$ are somewhat higher by the thermocouple measurements. This might be the result of one or more of several causes: (1) Lack of "blackness" of the radiation from the platinum strip, which would give pyrometer readings which are too low; (2) the surface of the platinum in the thermocouple measurements being colder than the center, would give a λ_{max} which is too large for the true temperature; (3) the greater roughness of the platinum surface in the thermocouple series would increase the "blackness" of the radiation, thus giving a λ_{max} which is too large.

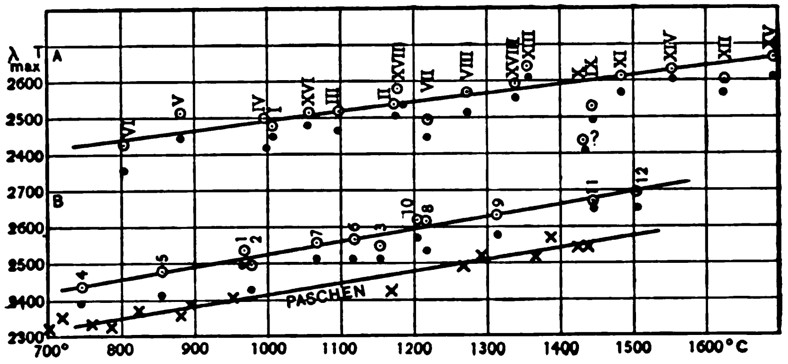

Fig. 3

The lack of "blackness" of the radiation from the V-shaped opening might have been tested by determining the melting point of the strip by means of the optical pyrometer. But the strip collapsed when heated above 1700°, and the nature of the radiating properties of platinum did not appear to warrant an attempt to establish accurate numerical values of these constants.

It is to be noticed that the values of α are obtained by a method which is independent of the temperature measurements. The mean value of α for a given temperature is not markedly different for the two methods of determination.

It is to be noticed that sometimes the same energy curve gave a good value of α and a poor value of $\lambda_{max}T$. This is owing to the fact that (e. g., the value of curve *X*, Fig. 3–*A*) the energy curve was poor in the region of 3μ to 5μ, which affected the λ_{max}, but was good in the region of 1μ to 2μ, from which region was obtained the value of E_{max} used in computing α.

The two independent methods used in investigating the so-called radiation constants (α, which is obtained without a knowledge of the temperature, and $\lambda_{max}T$) lead to the same conclusion that there are no real "constants" for metals (platinum), as announced in the previous communication. The value of $\alpha = 6$ and $\lambda_{max}T = 2600$ are therefore applicable only in work which does not require high accuracy.

It is purposed to inquire into the total radiation of metals to learn whether it is possible to obtain a more accurate temperature coefficient of emission for α than it is possible to obtain from the data herewith presented.

In conclusion, acknowledgment is due Mr. U. F. Rosen for the computations involved in this research, the experimental part of which was carried out about eight months ago.

II. EMISSION SPECTRA OF NEON, HELIUM, AND MERCURY

The spectral-energy distribution of the radiation from various gases in vacuum tubes and from metalic vapors in the carbon arc was given in a previous paper.[9] The main object of the investigation was to determine the location of the strongest emission lines in the spectrum. It was found that in all cases the most intense lines lie just beyond the red (in the region of 0.8μ to 1.0μ) and that in the region of 1.5μ to 3.5μ there was a complex radiation which was weak in intensity and, usually, unresolved with the spectrometric apparatus employed. Subsequent experimenters, using a larger dispersion, have succeeded in resolving this latter region into separate lines, which in their spectral-series relations are found to be a continuation of the lines in the visible spectrum. The dispersion of the present spectro-bolometric apparatus (mirror spectrometer, fluorite prism, and vacuum bolometer) was not sufficient to enable one to locate the individual lines. However, a vacuum tube containing neon being available, it was deemed of interest to continue the inquiry as to the location of the most intense emission lines. At the present stage of our knowledge of the subject but little can be said of the application of these data. The subject may be summarized by stating that in spark spectra the most intense lines are situated in the ultra-violet; that in arc and vacuum tube spectra the most intense lines are situated just beyond the red; and that in the spectra of solids the maximum emission lies far in the infra-red but shifts rapidly toward the visible with rise in temperature.

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[9] Physical Review, 22, p. 1; 1906. Carnegie Publication No. 35; 1909.

The prismatic (x x x) and the normal (. . .) spectral energy curves of neon are given in Fig. 4, from which it may be noticed that the maximum emission lies within the group of lines in the red of which the line at 0.64μ is the brightest to the eye. The intensity of the line or group of lines in the region of 0.8μ is only about one-twentieth that of the red. A slight emission was observed at 1.1μ. Beyond this point no radiation was observed for the current (0.008 ampere, capillary tube 1 mm diameter) at which the tube was operated. No doubt more lines will be observed on more intense excitation, but this will not modify the observations as to the location of the maximum emission. From the data at hand it appears that the maximum emission at 0.64μ is not due to the lack of resolution of a group of lines, as compared with the maximum at 0.86μ, but that it is a property of this gas. This appears to be the only gas on record in which this property obtains.

The spectrum of helium consists of fewer lines than that of neon, the most prominent one (visually) being the yellow line at 0.5876μ. Radiometrically, however, conditions are quite different. The red lines are then found to be as intense as the yellow line.

The most intense line lies at 1.083μ, as shown in Fig. 4. The intensity of a weak line at 2.05μ is only 0.05, and the yellow line (0.587μ) is only 0.1 the value of the line at 1.083μ.

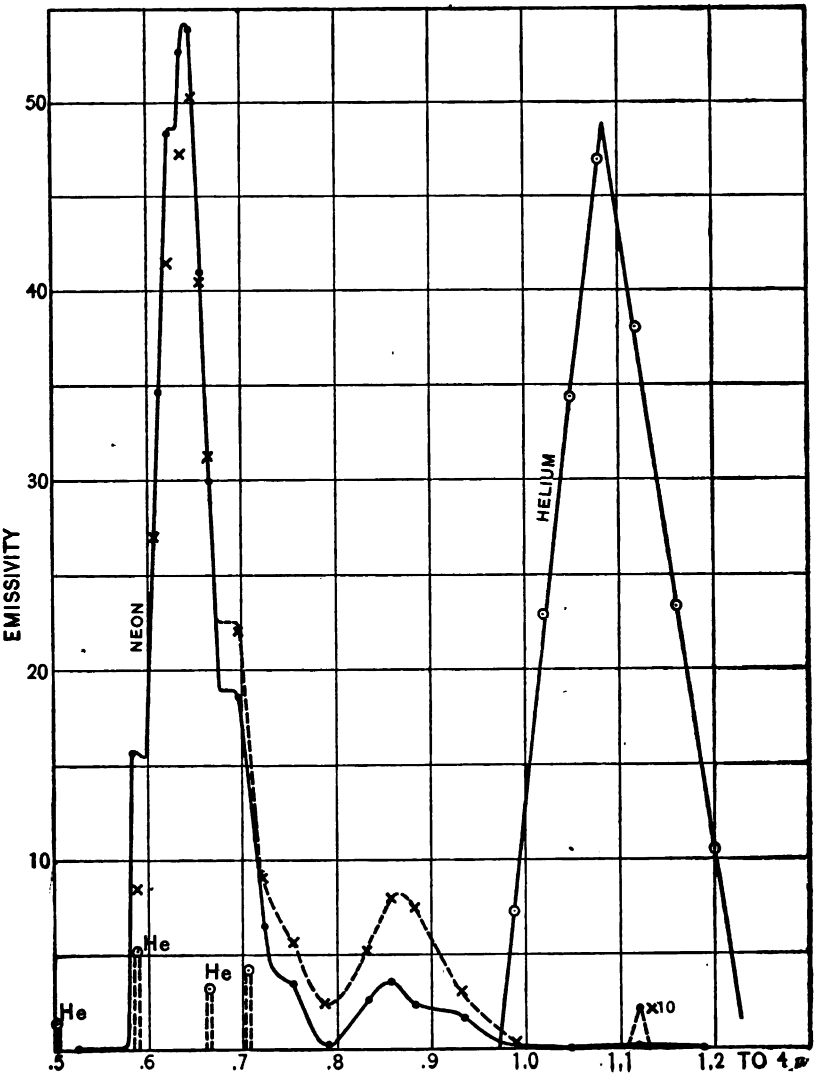

Fig. 4

It is well known that only a small fraction of the energy expended in such gases as helium, xenon, etc., is required to excite neon to light emission. Since the energy put into the gas must come out again in some manner (mostly as radiation of various wavelengths) and since but little of the radiation emitted by neon is in the infra-red, an explanation is at hand of the small energy input (high efficiency) required to excite this gas to light emission.

The luminous efficiency of vacuum tube radiation (air,[10] nitrogen, carbon dioxide, helium, etc.) is of the order of 15 to 20 per cent, or perhaps even much lower, owing to the great amount of infra-red radiations emitted. In marked contrast with these gases is neon, in which the infra-red is almost entirely absent, so that its luminous efficiency is of the order of 80 to 90 per cent. The color of this light is a rich crimson.

In conclusion, it may be noticed that the spectrum of neon is composed of numerous fine lines, more than 60 of which lie between the red and yellow helium lines (0.5876μ and 0.7065μ). With a larger dispersion the shape of the curve will necessarily change until, when final resolution is attained, each spectral line will give a more symmetrical energy curve, as observed (Fig. 4) at 1.083μ for helium. There is sufficient reason for believing that the emission lines in neon are just as numerous at 0.8μ to 1.0μ as they are in the visible spectrum, so that whatever the dispersion, the same energy distribution will obtain as here observed, viz, that the strongest lines occur in the region of 0.6μ to 0.7μ of the visible spectrum. In this respect, as already stated, neon is unique.

The prismatic energy distribution of a Heraeus quartz-mercury lamp is given in Fig. 5 for different values of energy consumption. The lamp used (end on) was of the 110-volt type, being 7 cm in length, the electrodes having cooling wings of thin sheet copper. With the fluorite prism and mirror spectrometer used in making the observations the green and yellow lines (0.546μ and 0.576μ, respectively) are completely resolved so that the relative intensities are as shown in Fig. 5. The two lines at 1.014μ and 1.128μ are not resolved, as shown in curve *a*, so that apparently the intensities are as great as is the yellow line. In the normal spectrum the intensities of these lines would be much less than one-fourth (slit width at 1.0μ is about 4 times the value at 0.58μ) the yellow line. The mercury spectrum is therefore similar to the neon spectrum in having the strongest emission lines in the visible spectrum.

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[10] Drew: Phys. Rev. 17, p. 321; 1903.

It is well known that the green mercury line is easily excited to light emission so that the hot mercury shaken back and forth in the quartz lamp emits a beautiful greenish light. On excitation the yellow line increases rapidly in intensity. This is well illustrated in Fig. 5. Using an energy input of 42 watts the green, the yellow, and the line at 1.01μ (unresolved), are of practically the same intensity. On 81 watts the yellow line is 1.4 times and on 103 watts it is 1.7 times the intensity of the green line (the observations are joined by dotted lines for convenience in illustration) while the infra-red grows in proportion with the yellow line. It is of course known from the work of Küsch and Retschinsky,[11] and of Pflüger[11] that lines belonging to a given

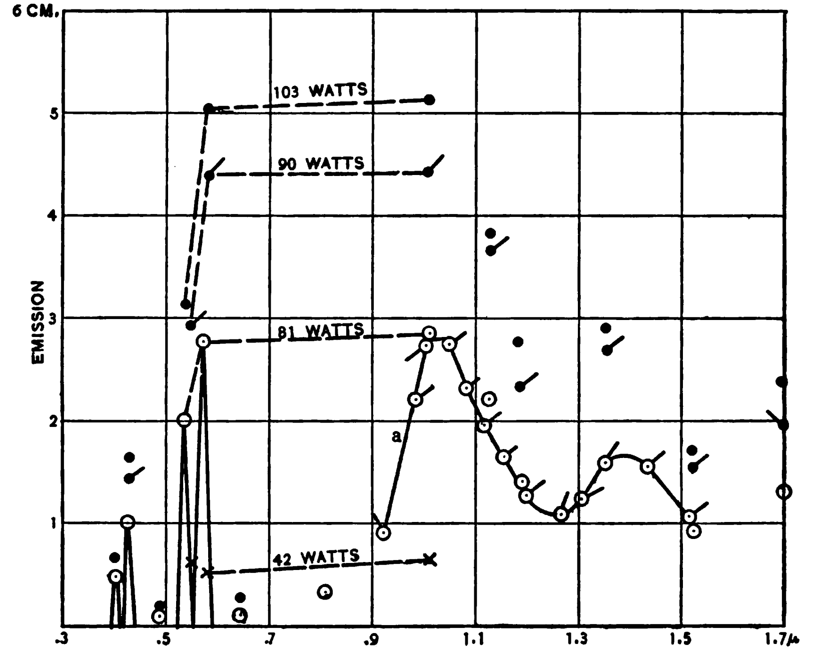

Fig. 5.—*Mercury vapor*

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[11] Küsch and Retschinsky: Ann. der Phys. (4), 20, p.563; 1906. Pflüger: Ann. der Phys. (4), 26, p. 789; 1908.

spectral series increase in intensity in the same proportion; and that for different spectral series lines the increase in intensity is different for the same energy input. The present data, however, furnish instructive information, not previously at hand, as to the cause of the decrease in luminous efficiency, after exceeding a given energy input, which according to Küsch and Retschinsky is about 0.18S w. p. m. h. c. This is owing to the rapid increase in intensity of the emission lines in the infra-red as compared with the blue and green lines. The intensity of the yellow line, increasing as it does in the same proportion as the infra-red, is not sufficient to counterbalance the loss by radiation in the infra-red, and the result is a decrease in the ratio of the luminous to the total radiation.

III. EMISSIVITY OF DIFFERENT PARTS OF AN ACETYLENE FLAME

In a previous paper [13] it was shown that in the spectral energy curve of an acetylene flame viewed flatwise, the maximum emission at 1.25μ is twice the height of the maximum at 4.35μ; and that for the flame viewed edgewise the ratio is 5.5. The emission maxima of the flame viewed edgewise are shifted about 0.05μ toward the longer wave lengths, viz, at 1.30μ and 4.40μ, respectively.

In the visible spectrum the spectral energy curves of the flame viewed flatwise and edgewise were found to be superposable, as one would expect; for the color of the flame appears to be independent of the thickness of the radiating layer.

In a subsequent examination made by Messrs. Beatty and Crittenden, using the same apparatus (vacuum bolometer, fluorite prism, and spectrometer) the spectral energy curve given in Fig. 6 was obtained. The lower part of the flame radiated flatwise into the spectrometer slit. The chief interest in this curve is that the maximum at 1.15μ which is caused by the radiation from the carbon particles is only about 0.7 the height of the CO_2 maximum at 4.35μ. The shift of the latter maximum from 4.40μ to 4.35μ is to be ascribed to a lower temperature; for the position of this maximum is a function of the temperature. The shift in the maximum from 1.25μ to 1.15μ is the result of the rapid decrease in emissivity with thickness of the radiating layer, in the spectral region from 1.5μ to 2.5μ, where the radiation is far less saturated than in the visible spectrum. This brings out the small emission band of CO_2 at 2.75μ which was obliterated by the more intense emission of the thicker radiating layer of carbon particles, observed in the previous paper. In Fig. 6 the crosses (x x x) illustrate the relative heights of these two emission maxima when the flame radiated edgewise into the spectrobolometer. Here the ratio of the two maxima is 3, as compared with the values of 0.7 to 2, when the flame was viewed flatwise.

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[13] This Bulletin, 7, p. 243; 1911.

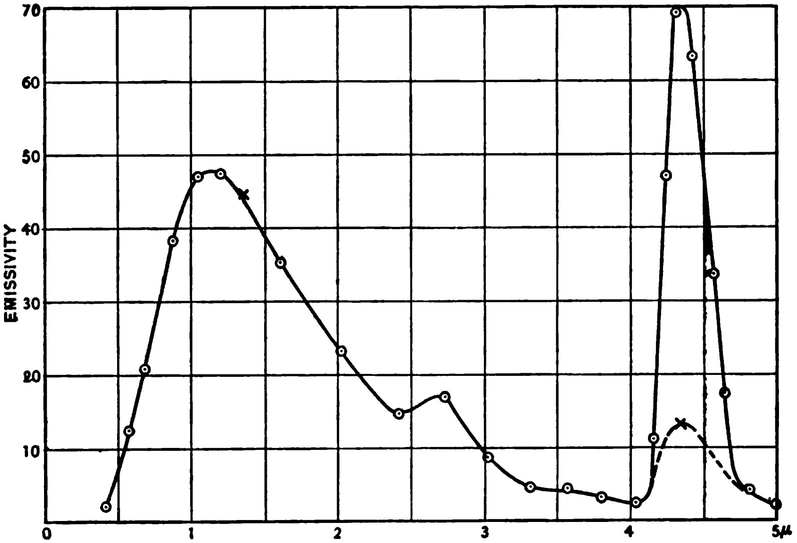

Fig. 6.—*Acetylene flame*

Evidently the wide variations in the radiant efficiency of the acetylene flame, as obtained by various observers by integrating the spectral energy curves, is to be explained on the basis of such evidence as herewith presented.

It was deemed of interest to investigate this subject further in connection with the question of the combustion of gases in flames. The question investigated was the relative intensities of these two maxima (carbon particles and carbon dioxide) in different regions of the flame. Because of the lack of intensity it is very difficult to observe the complete spectral energy curve of a small part of the flame. Accordingly only the (prismatic) maxima of emission were observed. A flat and a cylindrical flame were examined. In the burner used (Von Swarz "Perfection," previously described) the flat flame is produced by two cylindrical jets of ignited gas impinging at an angle of 90°. This leaves a (transparent) nonluminous region 4 to 5 mm in diameter at the base of the flame, as shown in Fig. 7–*A*.

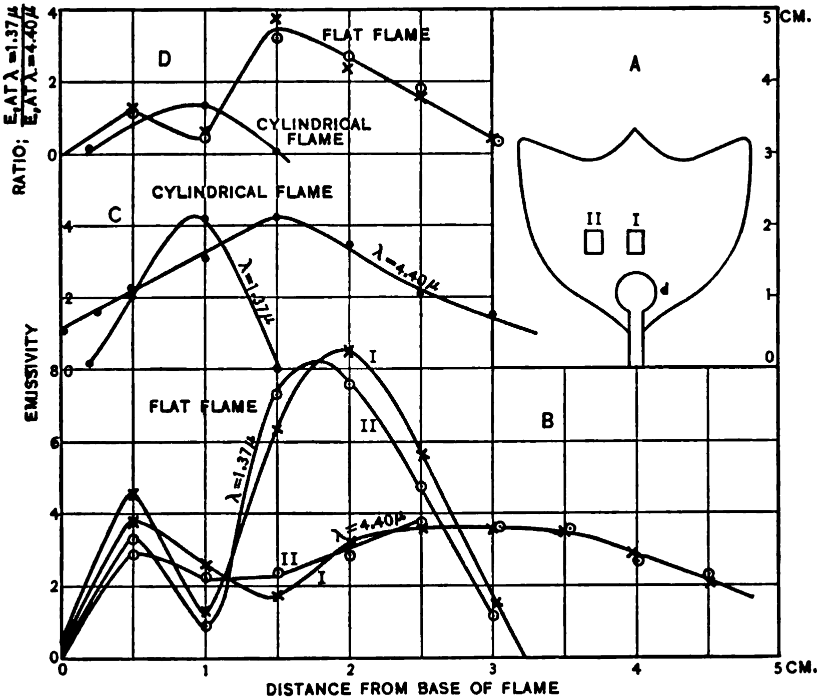

Fig. 7.—*Acetylene flame*

The flame was placed back of a metal screen with a hole in it 3 mm high and 2 mm wide. An image of the illuminated slit was projected upon the spectrometer slit by means of a short focus mirror. The flame was mounted upon a carrier having a graduated scale, which enabled the operator to raise or lower the flame before the opening in the metal screen.

Two series of observations were made on the flat flame on the regions shown by the small rectangles (I, II) in Fig. 7–*A*. Starting with the slit at the base of the flame, with the spectrobolometer set on $\lambda = 1.37\mu$ and gradually lowering the flame, a series of observations was made as shown in the lower part of Fig. 7–*B*. Resetting the flame (slit at the base of the flame) and placing the bolometer in the region of 4.40μ a similar series of observations was obtained. The first maximum emission, at 5 mm from the base of the flame, comes from the cylindrical jets, and the lowest emission comes from the dark spot, *d*, of the flame, Fig. 7–*A*. The carbon particles have their maximum emission 2 cm above the base while the CO_2 emission continues very strong several centimeters above the luminous flame. The minimum emission of the CO_2 at 4.40μ appears to be situated several millimeters above the nonluminous spot, *d*, Fig. 7–*A*.

The radiation from the cylindrical flame was similarly observed, Fig. 7–*C*. It is of interest to note that at the base, where combustion begins but where the flame is almost nonluminous, the CO_2 (CO ?) already emits considerable energy. Furthermore, the carbon particles emit but little in the hazy region 2 cm above the base, where the luminosity seems to be somewhat similar to the radiation from incandescent carbon dioxide in vacuum tubes. Of course there is no discontinuous spectrum as found in the vacuum tube discharge through CO_2. Perhaps it would therefore be better to consider this glow similar to the hazy outline at the base of a Bunsen flame. The CO_2 emission continues strong for some distance above the luminous part of the flame.

In the upper part of Fig. 7–*D* is given the ratio of emission of these two curves (7–*B* and 7–*C*; E at $1.37\mu \div E$ at 4.4μ)) from which it is easy to see how, in integrating over a large area as was done in obtaining the spectral energy curves of Fig. 6, the relative height of the two maxima depends upon the position of the flame before the slit.

The data at hand are too meager to consider the question of "luminescence" in the hazy luminous region at the top of the flame, where the emission of the carbon particles became immeasurably small. From this preliminary survey it appears highly desirable to have a more thorough examination of various kinds of flames.

IV. VARIATION OF EMISSIVITY WITH THICKNESS OF THE RADIATING LAYER—OXIDES

In a previous paper[13] experimental data were given on the radiating properties of various metals in which only the superficial conditions (refractive index, reflecting power, etc.) were involved.

In a later paper[14] experiments were described on the variation in the spectral emission with variation in thickness of the radiating layer, as exemplified in the acetylene flame and in the Welsbach mantle. Attention was called to the fact that in nonmetals the emissivity is dependent mainly upon the absorptivity which in turn depends upon the thickness of the radiating layer. The investigation included a study of the acetylene flame radiating flatwise and edgewise into the spectrobolometer; also the Welsbach mantle heated to incandescence in the usual way and the same material formed into a solid rod and heated electrically.

In connection with these experiments it was of course desirable to obtain quantitative data on the variation in emissivity of some (pure) oxides with thickness. For this purpose samples of the same kind of glower material, squirted into rods of various diameters, were prepared under standard conditions.

The glowers described in the present experiments were squirted and baked by the Westinghouse Nernst Lamp Co., after which suitable platinum terminals were attached and covered with regular glower paste. After this the glowers were seasoned by operating them at a high temperature for five to six hours. The lengths of the glowers, determined experimentally, were such that they could be started on a 118 volt a. c. circuit by preheating with a blast lamp. The generator (rotary converter) was operated on a storage battery to insure a constant voltage. The alternating current was used instead of direct current to avoid the transference of platinum from the terminals into the glower, which occurs with heavy glowers. Suitable ballast rheostats were placed in series with the glowers, the lengths of which varied from 8 mm for the one which was 0.385 mm diameter to 18 mm for the glower which was 2.150 mm diameter. After starting the glower, the terminal voltage dropped to 99 volts (0.20 ampere) for the thinnest glower, and to 70 volts (1.86 amperes) for the thickest glower. A voltmeter was kept across the terminals and an ammeter was in series with the glowers.

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[13] This Bulletin, 5, p. 339; 1909.

[14] This Bulletin, 7, p. 243; 1911.

All the glowers were set to the same emissivity against a standard Nernst glower which in previous work[14] had been set to the same color as a 1.2 w. p. m. h. c. tungsten lamp. By placing the thin glowers one at a time in front of a thick glower, which was kept at a constant voltage, it was an easy matter to vary the voltage of the former until they disappeared against the thick glower. In this calibration the glowers were set to the same emissivity by viewing them through red, green, and blue glass. Usually there was no marked variation in the voltage readings when making these settings, using differently colored glass.

All these glowers were intercompared at the completion of the investigation, and it was found that the calibration had not changed. This was to have been expected, for the filaments had been thoroughly seasoned and each one had been operated but a short time.

A number of experiments might be performed with these glowers. One might, for example, study the candle power, efficiency, etc. For the present, experiments were made only on the shape of the spectral energy curves as modified by the change in thickness of the radiating layer. This gives the loss in efficiency resulting from the preponderating increase in emission in the infra-red spectrum. (Other methods will be necessary to determine the losses by conduction.) For this purpose the glowers were adjusted at a suitable distance before the slit of the vacuum spectrobolometer. No attempt was made to secure the same solid angle of radiation upon the prism face, for all the glowers had been set to the same emissivity in the visible spectrum, by optical methods, and the only requirement was to use the glowers at the voltages observed in obtaining the same emissivity and to obtain suitable factors with which to superpose the spectral energy curves of the various glowers, in and near the visible spectrum.

The results are shown in Fig. 8, which gives the normal spectral energy distribution of the various glowers. For the thin glowers (1 to 4) the spectral energy curves superpose over practically the

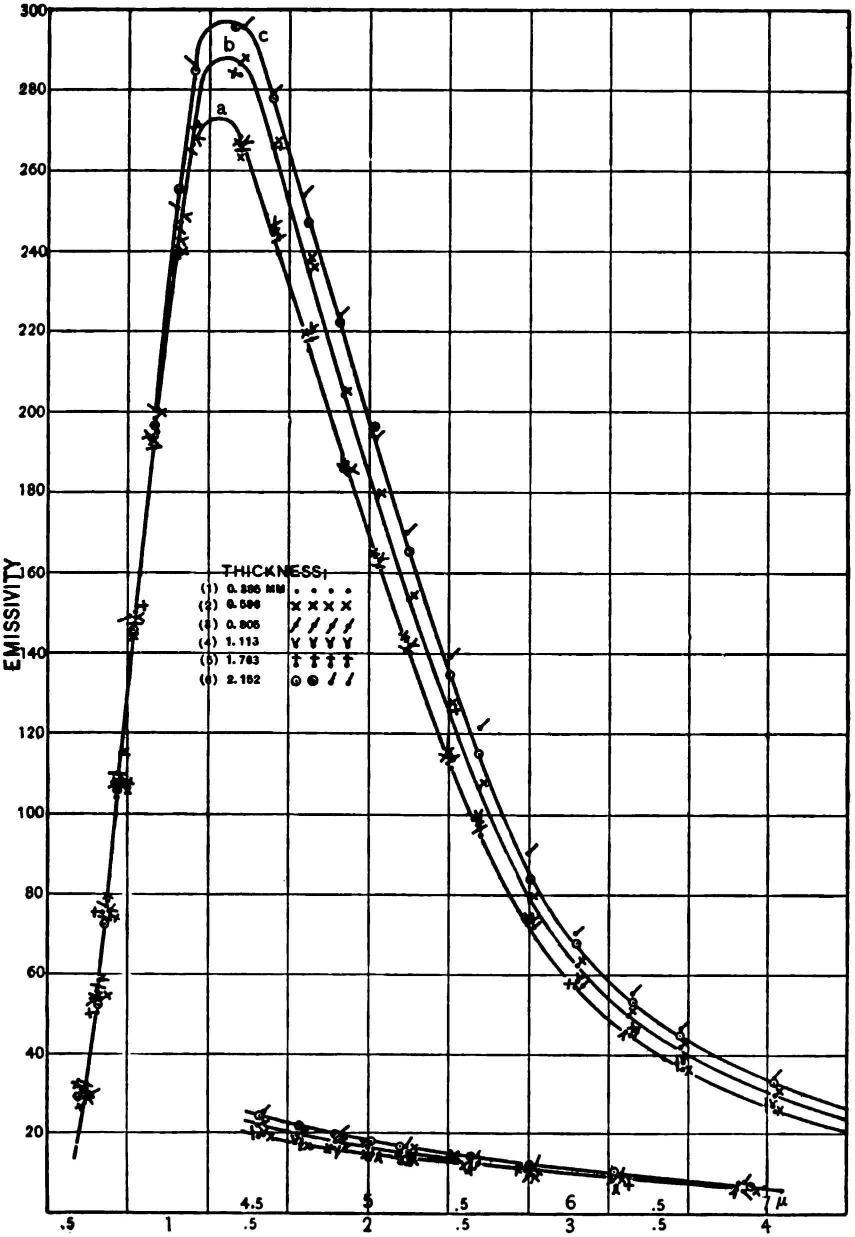

Fig. 8.—*Nernst glower*

whole length of the curve. The latter glower (4) shows a slight increase in emissivity at 1.5μ to 4μ. These form curve *a*, in Fig. 8. In curve *b* are given two series of observations on a glower 1.763 mm diameter. In the same manner, curve *c* shows two series of observations on a glower 2.152 mm in diameter, the observations being made on different days.

The increase in the emissivity, extending from 1.5μ to 6μ, is very marked in these two curves and is so great that it can not be attributed to experimental errors. An integration of these curves gives the ratio of the areas of $a : b : c = 1 : 1.071 : 1.134$. From this it appears that in order to obtain the same emissivity in the visible spectrum, the thickest filament radiates 13.4 per cent more infra-red energy than obtains in the thinnest filament. There is, of course, also a much greater loss of heat by conduction from the ends of the thick filament than from the thin filaments; but for the present the extent of this loss remains undetermined. The ordinary solid glower, 1.1 mm diameter, is represented by the higher values in curve *a*, which represents a loss of 2 per cent more infra-red radiation than obtains in the thinnest glowers.

The commercial A. C. glower is a hollow cylinder which is more efficient than a solid glower of the same diameter. To manufacturers it is a well-known fact that the very thin glowers are the most efficient. The data previously presented on the Welsbach mantle and the data herewith presented on the emissivity of various solid glowers show why this is the case. The efficiency can be increased somewhat by operating several glowers near together. This is owing to the fact that it requires about 18 to 20 watts to keep an ordinary 110-volt glower warm and conducting, unless operated on a high voltage transformer, as was found on a previous investigation of the selective emission[15] of the Nernst glower. The proximity of several glowers increases the surrounding temperature and decreases the losses by convection with a consequent rise in temperature for the same energy input.

The thicker the glower the more nearly its radiation approaches that of a black body. For the thinnest glower the maximum emission lies at about $\lambda_{max} = 1.25\mu$ and for the thickest filament the maximum emission is at about $\lambda_{max} = 1.32\mu$, although it is at the same emissivity in the visible.

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[15] This Bulletin, 4, p. 533; 1908.

The value of $\lambda_{max} = 1.32\mu$ and $\lambda_{max}T = 2930$ would make the temperature about 2230° Abs. No doubt the operating temperature is lower than this value, for the glower is not a black body as here assumed on the basis that the radiating layer is of sufficient thickness to emit completely all frequencies.

The above-mentioned filling up of the spectral energy curve between 1.5μ and 3μ, with increase in thickness of the radiating layer, is especially marked in the energy curve of the acetylene flame, an illustration of which is given on another page.

The data herewith presented confirms the previous conclusions that the radiation constant, α, of the Nernst glower varies with the thickness of the radiating layer.

V. RADIATION FROM A UNIFORMLY HEATED CAVITY AND FROM ITS INCLOSING WALLS

In the ideal radiator or so-called "black body" the walls of the inclosure are assumed to be opaque to all radiations. The energy emitted, of all wave lengths, is then independent of the nature of the material forming this opaque envelope. In practice such an opaque inclosure is not readily obtained and experimenters have to use radiators made of highly refractory porcelain, or graphite tubes, the latter being operated in a vacuum. Porcelain tubes may of course be blackened with nickel oxide, etc., but many objectionable features are then encountered.

During the course of experiments upon such radiators, in the construction of which every attempt was made to approach the ideal, the question arose as to whether or not the observed distribution of energy was independent of the composition of the radiating inclosure. Radiators constructed of ordinary porcelain appeared to have a slightly different spectral energy distribution from similar tubes of a more refractory "Marquardt" porcelain. The latter appeared to be slightly selective in its emission in the infra-red. When one considers the extraordinary way in which the frequencies emitted by the porcelain are modified when emitted from within the uniformly heated inclosure, the difficulties to be encountered in producing such a radiator become apparent. In Fig. 9, curve *a*, is shown the spectral energy distribution from the surface of a thin rod of Marquardt porcelain, rendered conducting

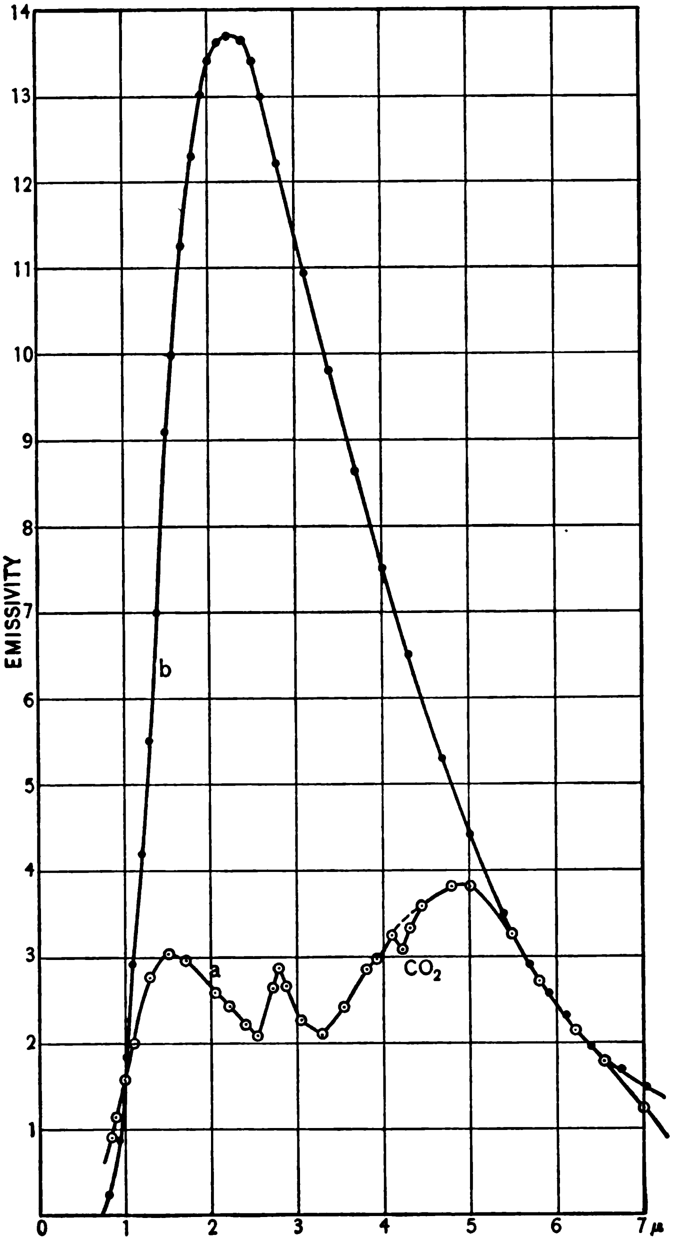

Fig. 9

by heating with a blast lamp and then heated to a bright red by means of an electric current from a 2000-volt transformer. There are three distinct emission bands. In this figure curve *b* represents the spectral energy distribution of the radiation from an experimental "black body" made of Marquardt porcelain and heated to 1032° C. The curve is perfectly smooth, but, in comparison with similar curves obtained from different "black bodies," made of a lower melting point porcelain, this curve appears to emit a slight excess of radiation in the region of 4μ to 5μ, as compared with the region of 3μ. Curve *a* is given simply as an illustration of an infinite number of curves, having different contours depending upon the composition of the material, and upon the temperature of operation, as was shown in previous investigations.

VI. STANDARD SPECTRAL ENERGY CURVES

In Table III are given the emissivities in the normal spectrum of a Nernst glower set to a color match with a tungsten lamp which was operated on 1.2 w. p. m. h. c. This is not far removed from the commercial operation of the Nernst glower. The glower (length 13 mm, diameter 1 mm, well seasoned and quite crystalline in appearance) was purchased about 5 years ago, hence of different stock from the others herein described. This fact, however, does not cause any difference in the emissivity in the visible spectrum, but there appears to be some difference in the infra-red where the emissivity appears to be as high as that of the 2 mm glower, Fig. 8, discussed on a previous page.

The spectral energy distribution from 0.45μ to 0.67μ of a tungsten lamp operated on 1.2 w. p. m. h. c. is given in Table III. The spectral energy curve was obtained with a mirror spectrometer and a fluorite prism. At some future time it is hoped to provide further and more accurate data in the violet, so that the whole may be used as a standard spectral energy curve, such as was given in a previous paper for acetylene,[16] see Table IV. In the infra-red, however, the variation of emissivity with thickness is too marked to permit the use of the acetylene flame as a standard of radiation.

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[16] This Bulletin, 7, p. 261; 1911.

The data in Table III are useful also in considering the minimum concentration of a solution of cupric chloride as a filter to absorb all the infra-red, as described on a subsequent page.

TABLE III

Spectral energy distribution from 0.45μ to 0.67μ of a tungsten lamp operated on 1.2 w. p. m. h. c. and of a Nernst glower from 0.45μ to 9.00μ set to a color match with the tungsten lamp

Wave length in μ=0.001 mm	Emissivity	Wave length in μ=0.001 mm	Emissivity
0.449	7.6	2.033	408.1
.466	10.8	2.189	345.2
.485	15.2	2.410	282.6
.506	20.4	2.546	250.1
.530	29.0	2.801	189.4
.558	40.4	3.037	140.9
.589	59.0	3.367	107.4
.606	73.0	3.569	83.6
.646	103.2	4.031	64.1
.697	151.5	4.445	49.2
.757	213.6	4.827	40.5
.835	311.9	5.485	30.2
.934	409.0	6.240	20.9
1.054	524.1	6.852	14.6
1.197	608.0	7.546	10.5
1.357	635.7	8.170	5.3
1.526	605.9	8.737	2.5
1.698	534.0	9.090	1.4
1.868	464.1		

TABLE IV

Spectral Energy Distribution of an Acetylene Flame

[Reprinted from Bulletin Bureau Standards, Vol. 7, p. 261, 1911]

Wave length in μ=0.001 mm	Emissivity	Wave length in μ=0.001 mm	Emissivity
0.36	3.5	0.56	43.7
.38	4.4	.58	54.0
.40	5.8	.60	66.3
.42	7.2	.62	80.5
.44	9.7	.64	96.5
.46	12.5	.66	112.8
.48	16.5	.68	130.1
.50	21.7	.70	147.0
.52	27.6	.72	163.8
.54	34.8	.74	181.5

The data in Table III on the Nernst glower show that this form of radiator can not be used as a standard of infra-red without rigorously defining the dimensions. There is also difficulty in defining the mode of operation of the glower; and in the present work it has been used by setting it to a color match with a tungsten lamp operated on 1.2 w. p. m. h. c. The latter may be easily rated photometrically.

As already mentioned, the glower used in obtaining the data in Table III was a well-seasoned one (made at least five years ago) which had a crystalline appearance, and it was 1.02 mm in diameter. The peculiar property of its energy curve is that it coincides throughout the spectrum with the energy curve of the glower of new material 2.152 mm in diameter, except at 2μ to 3μ, where the emissivity is higher than any of the glowers presented in Fig. 8. Whether this is the result of a difference in the composition of the material or in the physical structure is an interesting question. From the data presented in the previous paper on the Welsbach mantle material in the form of a solid rod, it appears that this difference in emissivity is owing to a difference in composition of the glowers. However, it is possible that with age the chemical structure of the material undergoes a change, which would produce a different radiating property of the material.

Note I.—LIGHT FILTERS WHICH ABSORB ALL THE INFRA-RED

Under the above title [17] experiments were described on the transmission of various solutions of copper salts, the object being to determine the minimum concentration which will absorb all the infra-red and at the same time give a high transmission in the visible spectrum.

Having in mind a discontinuous spectrum of the mercury vapor type in which the intensity of the radiation at 1.2μ is weak, a 2-cm layer of a 2 per cent solution of cupric chloride was recommended as being sufficiently opaque for eliminating the infra-red rays. Such a solution is of course inadequate as an absorption screen for eliminating all the invisible radiation from a source having an extremely large amount of infra-red such as obtains in incandescent solids of the Nernst glower type. On integrating the spectral energy curve of a Nernst glower (used on normal operation) after transmission through such a solution, it is found that the amount transmitted in the infra-red might cause an appreciable error in the measurement of the (total) radiation in the visible spectrum. Further experiments were therefore undertaken to determine the proper concentration which will reduce to a negligible quantity the energy transmitted in the infra-red.

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[17] This Bulletin, 7, p. 655; 1911.

In view of the fact that a copper sulphate solution changes from a bluish to a greenish yellow color on dilution, a further examination was made of this substance in solution to compare with cupric chloride in solution. It was found that a solution of copper sulphate of the same color as a 2.5 per cent solution of cupric chloride was considerably more transparent than the latter, in the region of 1.2μ. There is therefore no advantage in employing copper sulphate as a radiation filter for eliminating the infra-red.

The transmission of an accurately prepared 2.5 per cent solution of cupric chloride (2.5 grams $CuCl_2 + 2H_2O$ in 97.5 grams of water and 2 drops of HCl) is given in Fig. 10, the absorbing layer being exactly 2 cm in thickness, the cell walls being of clear white optical glass (each) 1 mm thick. An old and a newly prepared solution were examined. The maximum transmission at 1.15μ to 1.20μ is of the order of 0.35 per cent. The transparency was slightly increased on adding several drops of HCl. The depression at 0.51μ is caused by the dichroism of the solution.

The transmission of an accurately prepared 3 per cent solution (3 gr $CuCl_2 + 2H_2O$ in 97 grams of water and 2 drops of HCl) is also given in Fig. 10. The maximum transmission at 1.2μ is of the order of 0.16 per cent, with a possibility that the value is still lower. Using a 3.5 per cent solution of $CuCl_2$ (3.5 gr $CuCl_2$, 96.5 gr H_2O, and 2 drops of HCl), the infra-red spectral energy curve of the Nernst glower is reduced to a narrow band at 1.2μ, Fig. 10, which is entirely negligible in comparison with the curve of the visible spectrum.

Fortunately in the case where green and violet radiation are desired a still more concentrated solution (say 4 per cent) may be employed, which eliminates the infra-red still more completely.

This is an important fact, for a small amount of infra-red added to the green and blue radiations, which have a low energy value, may cause an appreciable error. On the other hand, when it is desired to obtain considerable radiation in the yellow and orange, because of the high energy value of these radiations, the use of a weaker solution (3.5 per cent) is permissible, since the slight addition of infra-red is negligible in comparison with total energy to be measured.

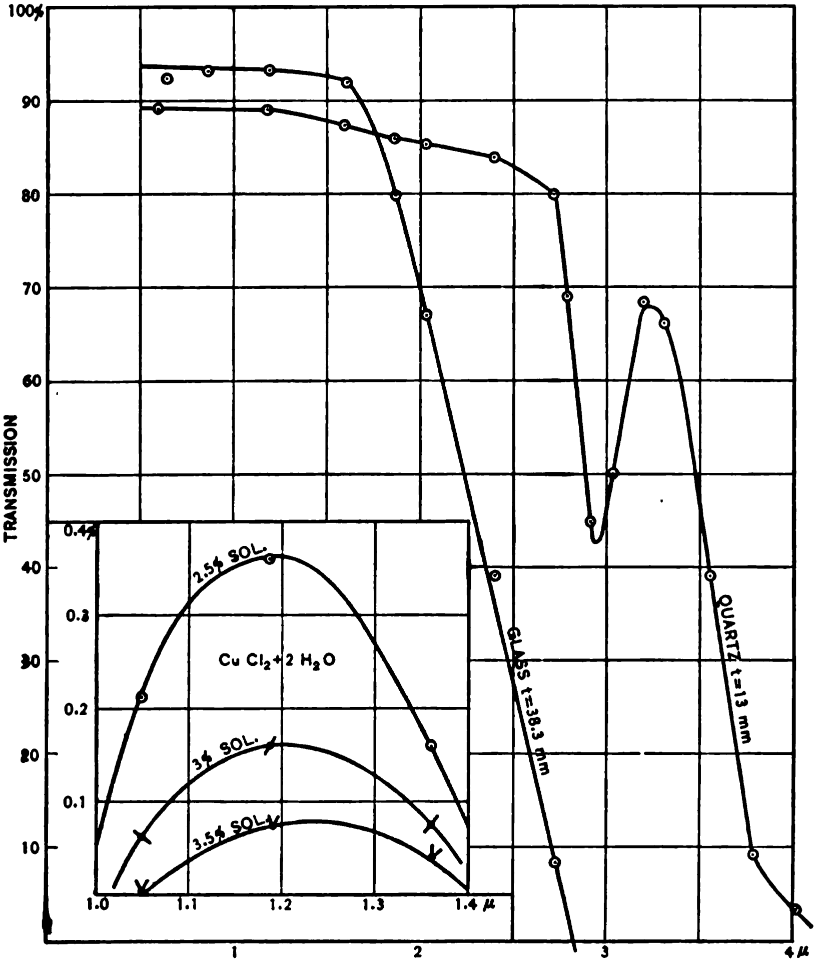

Fig. 10

TABLE V

Concentration of solution	2.5%	3.0%	3.5%
λ		**Ratio of energy transmitted**	
1.05μ	0.0021	0.0006	0.00003
1.20μ	0.0036	0.0016	0.00075
1.36μ	0.0015	0.0007	0.00040

It is of course to be understood that this screen is useful only to eliminate the infra-red and that, in order to obtain red, green, or blue, etc., it is necessary to use a suitable monochromatic color screen in addition to the aforesaid standard solution of cupric chloride.

During the course of these experiments a number of samples of (old and new) 3 per cent solution were examined, all of which gave nearly the same transmission, showing that by exercising care in preparing these solutions there will be no marked uncertainity as to the amount of infra-red radiation that is transmitted. The use of more concentrated solutions is of course to be recommended whenever the nature of the problem permits it. The present experiments simply show the minimum concentration and permit a calculation of the error from infra-red radiation, provided the spectral energy curve is known. For this purpose is included the transmission (Figs. 10 and 11, and Tables III and V) of the solutions of cupric chloride, just described, the absorption cell being exactly 20 mm thick. For determining these ratios a Nernst glower was used as a source of radiation. The glower was set to the proper voltage (practically on normal operation) to give a color match with a tungsten lamp operated on 1.2 w. p. m. h. c. The galvanometer deflections in the region of 1.0μ to 1.3μ without the absorption cell were equivalent to 8000 to 11 000 mm, and through the solution they were from 0.2 to 6 mm. Only the great steadiness of the vacuum bolometer permitted measurements of such small magnitudes as were observed through the solutions. In Fig. 11 is shown the spectral energy curve as observed through the solutions just described. For the 3 per cent solution the total energy transmitted in the region of 1.05μ to 1.35μ is 4 per cent of the energy transmitted in the visible spectrum, from 0.44μ to

0.68μ. The energy transmitted at 1.05μ to 1.35μ by a 3.5 per cent solution of $CuCl_2$ is less than 1 per cent of the energy transmitted in the visible spectrum. Whether the infra-red can be separated as thoroughly from the visible spectrum by mechanical means (Ångström's knife-edge screen) as by this method, remains undertermined. Possibly a combination of the two methods would be still better, for in this case a weaker solution could be used to eliminate the infra-red rays scattered over the spectrum by the screen. In this case the screen would not have to be set

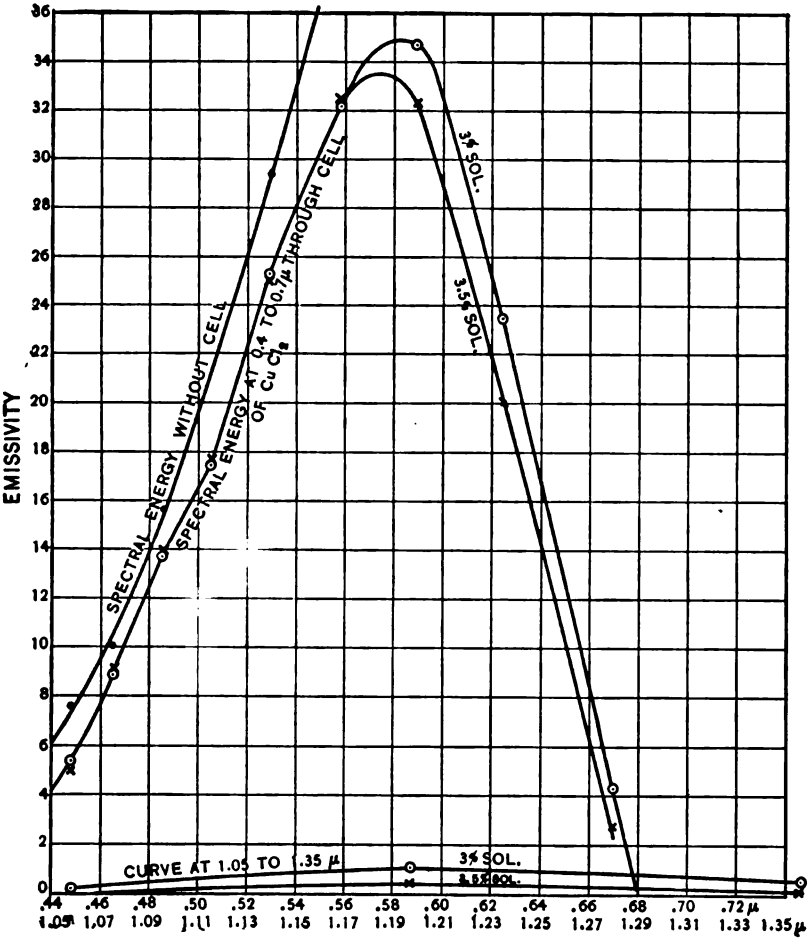

Fig. 11.—*Nernst glower*

so accurately at 0.7μ to separate the infra-red from the visible, for the solution would absorb the radiations lying between 0.7μ and 0.9μ and the small amount remaining of the radiations at 1.05μ to 1.35μ would be situated so far from the edge of the screen that none could pass by and into the radiometer.

From the data herewith presented it is evident that for sources of radiation having a high emissivity at 1.2μ to 1.5μ the 2 per cent solution of $CuCl_2$ described in the previous paper is not sufficient to eliminate to a negligible amount all the infra-red; that a 3.5 per cent solution is necessary to reduce the infra-red to 1 per cent of the visible radiations; and that for producing green and blue radiations it is desirable to eliminate the infra-red still further by using a solution of 4 per cent of cupric chloride.

In conclusion it is desirable to emphasize the importance of using exactly the same thickness 20.0 mm to obtain the results herewith presented. For example a cell 21 mm in thickness of a 2.5 per cent solution transmits 0.28 to 0.30 per cent as compared with a transmission of 0.35 per cent by the 20-mm cell, see Table V, which gives the ratios of the energy transmitted by the solution to the direct radiation falling upon the radiometer.

Ångström separated the visible spectrum from the infra-red by means of a knife-edge screen. One objection to this method is the uncertainty as to the amount of stray infra-red, especially of wave lengths just beyond the visible, that is superposed upon the visible spectrum. As already mentioned a combination of Ångström's spectrum knife-edge screeh and a weak (1 per cent) solution of $CuCl_2$ would remedy this defect without seriously reducing the intensity in the red. The amount of infra-red transmitted by this solution at 1μ is so small and it is located so far from the edge of the screen that there is no danger of an appreciable amount of infra-red being superposed upon the visible spectrum.

As a final summary it may be stated that the method of obtaining monochromatic radiation by means of filters is very inefficient when concentrated solutions must be employed. For example, the 3 per cent solution transmits 58 per cent, and the 3.5 per cent solution transmits only 55 per cent at 0.589μ. The transmission is, of course, much higher in the blue and in the green.

Note II.—TRANSMISSION OF PRISM MATERIAL

In order to learn the applicability of glass and quartz prisms in spectral energy work at high temperatures, the transmission of thick samples of these materials was examined, as shown in Fig. 10.

The plate of quartz, 13 mm in thickness, increases rapidly in opacity beyond 1.2μ, so that it is unsuitable in spectral energy work (other than isochromatics) involving wave lengths greater than 1.2μ. The same is true of crown glass, the transmission of which is shown in Fig. 10, thickness 38.3 mm.

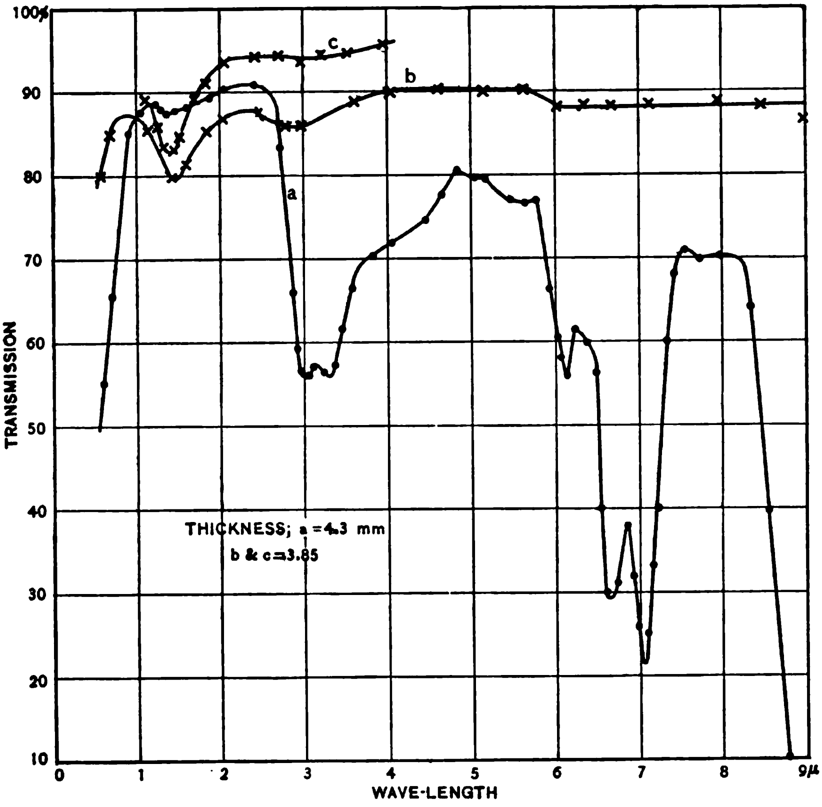

Fig. 12.—*Fluorite*

Owing to the increased scarcity of fluorite it is important to learn the utility of the green varieties of this material. In Fig. 12, *a* is shown the transmission of a sample of deep green fluorite

(4.3 mm in thickness) which showed a strong violet fluorescence in ordinary light. The transmission curve is conspicuous for numerous absorption bands, the maxima of which occur at 1.4, 3.0, 3.3, 4.2, 5.6, 6.1, 6.63, 7.03μ, respectively. The transmission of a light yellowish green sample is shown in Fig. 12, *b* and *c*. Here the prominent bands at 3μ and 7μ appear to be entirely absent, while the band at 1.4μ is very marked as compared with a similar absorption band in the deep green sample.

WASHINGTON, June 5, 1912.

ON A MODIFIED FORM OF STABILITY TEST FOR SMOKELESS POWDER AND SIMILAR MATERIALS

By H. C. P. Weber

Some time ago an investigation on the stability of nitrocellulose plastics was undertaken at the Bureau of Standards, and the question of the stability of these materials at normal and elevated temperatures was one of the questions studied.

One of the stability tests employed in that investigation seems of sufficient interest to warrant calling attention to it, especially since it does not seem possible to carry the investigation further at present.

The papers to which reference has been made in connection with this subject are tabulated at the end of this paper and will not be cited again in detail.

There is, perhaps, no need for going into details regarding all the various tests proposed. While there are many of them, each having its own particular advantage, only a few are at all generally applied. The reason for adding to their number is that while this test is an explosion test, and therefore simple and rapid, it is in reality a determination of the change of decomposition velocity with rise in temperature and, as such, a measure of stability.

Various investigators have touched upon the influence of the rate of heating on the result, whether it be in the explosion tests or in methods depending on the amount or rate of gas evolution. For this reason the rate of heating in the explosion test is defined within certain limits. The decomposition of nitrocellulose is autocatalytic, and when a certain surrounding temperature is attained, say 135° C, nearly all samples of nitrocellulose will explode if kept in surroundings of that temperature long enough. The temperature of the decomposing material may be a few or many degrees above 135°. In the investigation of nitrocellulose plastics we have repeatedly seen differences of 30° and 40° between the temperature of the surroundings and of the sample when the substance went off. The amount of this difference depends on the mass of the material and its heat conductivity and on the heat conductivity of the system used for test. These factors enter into the German 135° test as well as into the ordinary high temperature explosion test. In the former the time will vary with the heat insulation; in the latter the explosion temperature will vary with the rate of heating.

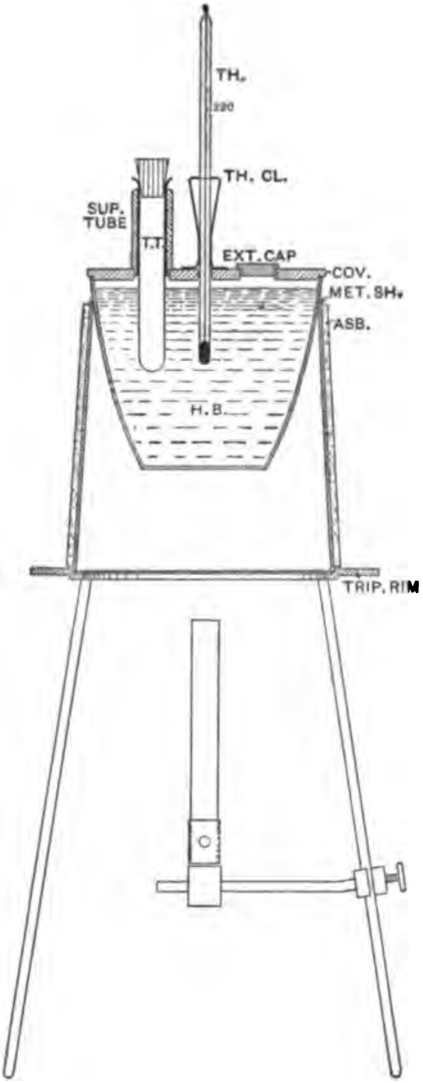

Fig. 1

The apparatus used for the test is shown in Fig. 1. The heating bath consists of a crucible of iron or nickel, about 10 cm in diameter and of approximately the same depth. The cover is of sheet metal, about 3 mm thick, with a flange that fits snugly into the crucible and projects slightly beyond the rim. One hole through the center of the cover is just large enough to permit the thermometer to pass. Symmetrically distributed around the center of the plate are eight openings 15 mm in diameter. The heavy metal supporting tubes are about 4 cm in length and about 12 mm internal diameter. The lower end of the tube is flanged, so that the tube rests securely on the cover. The test tubes are about 9 cm long and must be of such diameter that they will just slip freely into the supporting tubes. A number of extra caps are provided to cover openings not intended to be used during the test. The heating liquid may be either paraffin, glycerin, or similar inert liquid, which may be heated to 200° without boiling or fuming strongly.[1]

The test tubes should dip about 4 or 5 cm into the heated liquid, so that their ends will be at about the center of the heated mass and may readily be removed one at a time and replaced by fresh ones. For each explosion a clean tube should be taken.

The thermometer is supported by a metal clip which rests on the cover, the bulb being on a level with the lower ends of the test tubes. The thermometer used was standardized. Since the mercury thread projected but little above the highly heated zone, the stem correction was found to be negligible. This should be checked with each apparatus and thermometer for the various temperatures when the apparatus is put together.

The heating bath is suspended in a conical piece of sheet metal wrapped with asbestos. The metal shield (Met. Sh.) is cut so that the crucible will hang securely in the upper smaller opening, while its larger end rests in the flanged tripod rim. With this apparatus and a small gas flame it has been easily possible to maintain the temperature constant for 15 or 20 minutes within half a degree. It is most convenient to have the burner set so that there is a tendency for the temperature to fall and to use a small accessory flame momentarily whenever necessary. With a temperature regulator or with electrical heating the ease of manipulation might, no doubt, be increased.

One or two stop watches[2] complete the equipment. When the apparatus has attained equilibrium at the desired temperature, one or more of the test tubes is loaded by dropping in the sample of powder, the stop watch is started, and a cork is dropped into the mouth of the test tube. The time until the explosion takes place is then noted.

The grains of the 6-pounder smokeless powder are of convenient size to use directly. Powders of larger caliber should be cut into pieces weighing about 0.2 g each. Each sample of powder was tested at four temperatures, 160°, 170°, 180°, and 200°. For the present purpose at least three tests were made at each temperature interval and a curve was drawn through the average values.

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[1] This form of apparatus has been devised by C. E. Waters in connection with work on lubricating oils.

[2] I have found the type of stop watch with two second hands, which may be stopped independently, the most convenient form. With two of these at least four samples may be observed simultaneously.

The following series on powder A shows how closely duplicates may be expected to agree:

						Av.	Max. Var.
200° C.	1′ 44″;	1′ 48″;	1′ 44″;	1′ 48″;	1′ 45″	1′ 46″	± 2%
180°	2′ 55″;	3′ 06″;	3′ 10″;			3′ 04″	− 5%
170°	4′ 17″;	4′ 30″;	4′ 28″			4′ 25″	− 3%
160°	14′ 20″;	17′ 40″;	17′ 34″			16′ 36″	−14%

In general the discrepancies appear to be greater at the lower temperatures. This is to be expected, since the curves given further on show to what extent the influence of small temperature variations is magnified in the region of 160°. Furthermore, the irregularities are more pronounced in the "poor" powders.

The following set shows what can be expected as to reproducibility of the complete curve. The sample used was L and the second test was made one month later than the first. The averages only are given:

	200° C	180° C	170° C	160° C
I	1′ 31″	2′ 18″	3′ 39″	7′ 11″
II	1′ 27″	2′ 31″	3′ 43″	7′ 30″

The following table and Fig. 2 give the results obtained with 10 samples of smokeless powder and two samples of nitrocellulose. The samples were obtained through the Navy Department, and I am indebted to the courtesy of G. W. Patterson, powder expert at Indian Head, for the selection of three classes, good, fair, and poor, and for the description of these samples, which I quote for comparison with the explosion periods:

Nitrocellulose A.—"Specially prepared. Heat test, potassium-iodide starch, at 65°5 C, 4 minutes; German test at 135° C, 9 minutes for litmus red."

Nitrocellulose B.—"Heat test, potassium-iodide starch, at 65°5 C, 42 minutes. German test at 135° C, 38 minutes for litmus red."

Powder Sample A.—"Six-pounder. Diphenylamine as stabilizer. German test at 135° C, litmus red, 2 hours 35 minutes, explosion 5 hours plus. Surveillance test at 80° C, 87 days; at 65°5 C, 307 days."

Sample B.—"Medium caliber. Diphenylamine as stabilizer. German test at 135° C, litmus red, 2 hours 17 minutes, explosion 5 hours plus. Surveillance test at 65°5 C, 271 days."

Sample C.—"Large caliber. Diphenylamine as stabilizer. German test at 135° C, litmus red, 1 hour 25 minutes, explosion 5 hours plus. Surveillance test at 65°5 C, 245 days plus."

Sample D.—"Large caliber. No stabilizer. Rosaniline as indicator. German test at 135° C, litmus red, 2 hours, explosion 5 hours plus. Surveillance test at 65°5 C, 60 days."

Sample E.—"Medium caliber. No stabilizer. Rosaniline as indicator. German test at 135° C, litmus red, 1 hour 35 minutes, explosion 5 hours plus. Surveillance test at 65°5 C, 74 days."

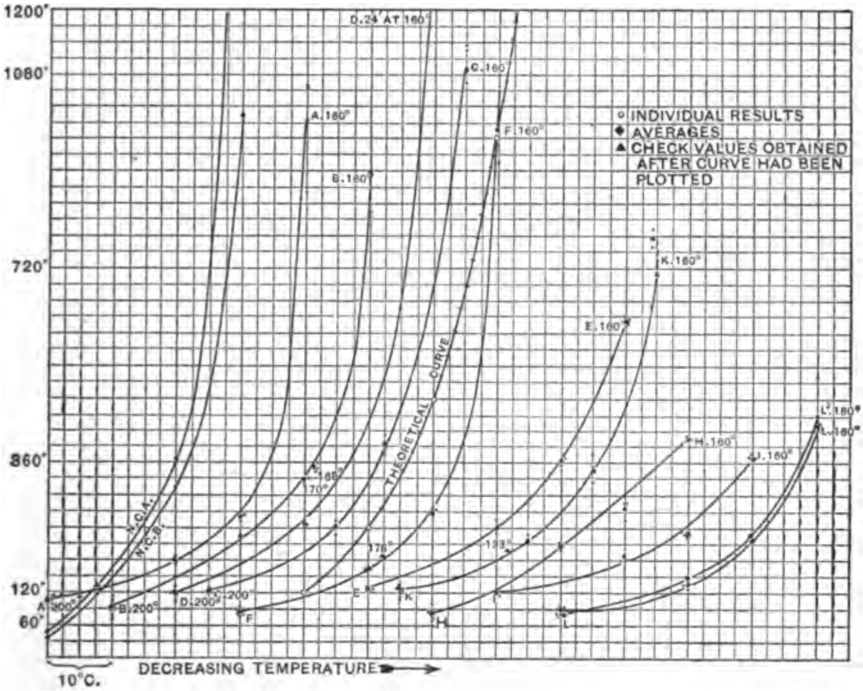

Fig. 2

Sample F.—"Six-pounder. Contains rosaniline and diphenylamine. German test at 135° C, litmus red, 2 hours 25 minutes, explosion 5 hours plus. Surveillance test at 65°5 C, 375 days; at 80° C, 64 days."

Sample H.—"Manufactured in 1901. When last tested it gave German test at 135° C, explosion in 41 minutes. Surveillance test at 65°5 C (1907), 79 days."

Sample I.—"Manufactured about 1901. When last tested, it gave German test at 135° C, explosion in 33 minutes; surveillance test at 65.5° C, 82 days."

Samples K and L.—"These are both in very poor condition, giving only one day surveillance test."

The explosion periods obtained on these samples are as follows. The value underscored is the average value.

Explosion Periods

Temperature	200° C	180° C	170° C		160° C
Nitrocellulose:	min. sec.	min. sec.	min. sec.	min. sec.	min. sec.
A	33	5 20	30+		30+
	58	6 11			
	37	6 56			
	·43	6 19			
B	33	4 06	16 00		30+
	42	5 55	17 30		
	34	6 06	16 45		
	36	5 22			
Powder:					
A	1 44	2 58	4 30		14 20
	1 48	3 06	4 17		17 40
	1 44	3 10	4 28		17 34
	1 48	3 04	4 25		16 36
	1 45				
	1 46				
B	1 54	3 37	5 23	5 44	14 20
	1 15	3 54	5 26	6 02	13 45
	1 65	3 44	5 36	5 53	17 7
	1 32	3 27	5 28	5 57	14 57
	1 33	3 57			
	1 41	3 44		168°	
	1 37				
	1 27				
	1 25				
	1 36				
C	2 04	4 05	6 17		17 45
	2 04	3 15	6 28		18 25
	2 10	4 50	6 55		18 18
	2 06	4 05	6 34		18 09
D	1 45	4 20	6 15	7 00	19 00
	1 47	4 03	5 53	6 50	26 49
	2	4 08	5 57	6 56	28 30
	1 58	4 10	6	6 56	24 46
	2 10				
	2 30		172°	171°	
	2 00				
E	1 35	3 55	6 10		10 15
	2 10	4 06	5 58		10 34
	2 10	4 18	6 08		10 29
	2 05	4 06	6 05		10 23
	2 10				
	2 10				

Explosion Periods—Continued

Temperature	200° C	180° C	170° C	170° C	160° C
Powder—Continued	*min. sec.*	*min. sec.*	*min. sec.*	*min. scs.*	*min. sec.*
F	1 40	2 47	3 33		15 16
	1 41	2 45	3 23		15 47
	1 48	2 49	3 31		17 40
	1 45	2 47	3 29		16 14
	1 45				
	1 38				
	1 43				
H	1 15	3 32	4 45		6 47
	1 29	3 35	4 17		6 48
	1 10	3 28	4 44		6 50
	1 15	3 32	4 35		6 48
	1 38				
	1 22				
	1 28				
I	2 04	3 05	3 50		6 13
	2 10	3 05	3 49		6 00
	2 02	3 20	3 56		6 17
	2 00	3 10	3 50		6 10
	2 05				
	2 05				
	2 04				
K	2 05	3 29	5 55		11 12
	2 05	3 30	5 22		11 8
	2 14	3 50	6 15		12 38
	2 17	3 36	5 51		11 00
	1 50				12 28
	1 52				13 00
	2 04				11 54
L	1 31	2 13	3 38		7 02
	1 22	2 18	3 33		7 12
	1 27	2 22	3 47		7 20
	1 35	2 18	3 39		7 11
	1 30				
	1 40				
	1 31				

K, at 183°, 3–20, 3–29; at 160°, 12–43, 13–20 minutes and seconds.
F, at 178°, 3–00, 3–13 minutes and seconds.
A, at 199°, 1–47; at 198°, 1–53; at 197°, 1–52; at 195°, 1–56; at 193.5°, 2–12 minutes and seconds.

The curves embodying these results are given in fig. 2. The curve marked "theoretical curve" is obtained on the assumption that the reaction velocity doubles for every 10° C. While the curves obtained from the explosion periods are of the same general type, it is apparent that the relation is not so simple as that shown by the "theoretical curve." What influence the stabilizer has upon the direction of the curves it is difficult to say with the data at hand. It does not follow that the stabilizer will affect the explosion test in the same manner as it does the heat test or the surveillance test. The stabilizer, while it removes the products of decomposition, may of itself act as a positive or negative catalyzer. If the decomposition be considered as the dissociation of an ester, the presence of a substance removing the products of decomposition will increase the rate. This has been noticed by Mittasch[8] for nitrocellulose with various basic additions and has been confirmed by myself in the case of pyroxyline plastics containing zinc oxide.

That the curves do actually represent the stability of the powder with changing temperature and are not accidental is shown by the reproducibility of the various points along the curve, as shown in the table; by the fact that the curve having been determined by four points, determinations made at varying temperatures are found to fall on the curve; and by the fact that the complete curve can be reproduced at widely varying intervals. (See curves L′ and L″.) The curves are undoubtedly characteristic for the sample. The deviations for individual points are not large enough to affect the general trend of the curve. What temperatures are chosen must probably be left to individual requirements; 190° would perhaps be preferable to 200°. At 150° we should have the apparent advantage that the differences between various samples become greater and the disadvantage that the test becomes slower and the results are more subject to accidental influences. The bend of the curve between 180° C and 160° C is, perhaps, its most characteristic portion.

The curves fall into three distinct groups for the samples tested, corresponding to their general classification of good, fair, and bad. The stable powders have a pronounced bend, while the ratio of explosion periods at 200° C and 160° C is at least 2:9. In the unstable samples this ratio falls as low as 2:3, and the points do not fit a smooth curve so well. The curves for the two samples of raw nitrocellulose are somewhat peculiar, being much flatter and corresponding more nearly to the theoretical curve.

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[8] Loc. cit.

The powders do not always fall in exactly the same order by this explosion test as they do by the surveillance or the heat test, but I think this is true to the same extent for the 135° German explosion test and the ones mentioned. This appears by comparison of the customary tests on samples D and H:

D, German test 135° litmus red 2 hours, explosion 5 hours; surveillance 60.
H, German test; explosion 41 minutes; surveillance 79.

From the results given it is evident that one explosion temperature, even if time is considered, does not give much information, while the determination of the characteristic curve does yield definite and specific information.

On account of the complexity of the conditions the test can hardly be expected to tell all that is to be known, but I believe that with sufficient data it may even be made to throw some light on the actual effect of the stabilizer on the natural decomposition velocity of the powder, as distinguished from the length of time before the decomposition products become noticeable.

CONCLUSION

The proposed method gives more accurate determinations of the explosion temperature than the method of heating with rising temperature.

It gives a better comparison of the relative stability of explosive substances.

The test is in effect a determination of the rate of change of decomposition velocity with change of temperature and is as such characteristic for each sample.

WASHINGTON, June 22, 1912.

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THE ATOMIC WEIGHT OF BROMINE

By H. C. P. Weber

INTRODUCTION

A considerable amount of work has been done in order to determine the atomic weight of bromine, and the oft repeated comparison of the atomic weights of silver and bromine makes it seem that this ratio is known with considerable accuracy. The value accepted for bromine, however, rests almost entirely upon that of silver, and it is of interest and importance to obtain a ratio between it and some other element. For chlorine a number of determinations of the ratio of hydrogen to chlorine in hydrochloric acid have been made, both by purely physical and by chemical methods. For bromine similar comparisons have not been made. Since the determination of the ratio chlorine : hydrogen was carried out with reasonable ease, it seemed probable that the method might be advantageously applied for the purpose of determining the ratio between hydrogen and bromine.

The method which was employed by Noyes and Weber[1] was found to give good results in this case. The initial difficulties to be overcome were somewhat greater, which was rather unexpected. They were largely due to the physical properties of hydrobromic acid gas and were eliminated after the method had been studied for some time and slight alterations in the method of manipulation had been introduced.

It is not necessary to go into a discussion of previous work on bromine here. The entire subject matter is to be found either in Clarke's "A Recalculation of the Atomic Weights"[2] or in Abegg's Handbuch, in the chapter on "Fundamental atomic weights."[3]

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[1] This Bulletin, 4, p. 345; 1908. (Reprint No. 81); J. Am. Chem. Soc. 30, p. 13; 1908.

[2] Constants of Nature, Part 5, Smithsonian Publication 1923; 1910.

[3] Abegg, Handbuch der Anorganischen Chemie., vol. 2, I; 1905.

The values which we have for bromine have been determined from the following ratios. The values here given are as given by Clarke, with one or two exceptions.

$KBrO_3$: KBr (Marignac), 80.291.

$AgBrO_3$: AgBr (Stas), 80.004.

Ag : Br (Marignac; Stas; Huntington; Richards; Richards, Collins, and Heimrod; Scott; and Baxter). In addition to these a considerable number of determinations have been made incidental to other work. These all taken together give a mean of 79.918.

AgCl : AgBr (Dumas, Baxter), 79.919.

Ag : KBr (Marignac; Stas; Dean; Richards and Mueller), 79.901.

AgBr : KBr (Richards and Mueller) (K=39.10), 79.903.

Ag : NH_4Br (Scott, Stas), 79.935.

Ag : NaBr (Stas) (if Na=23), 79.961.

These values are calculated on the basis silver=107.88. From the determination of the ratio Na : Cl and Na : Br by Goldbaum,[4] the value Br becomes 79.927 if sodium is taken as 23.00 and chlorine as 35.462. The value calculated by Clarke from all these determinations is 79.9197.

PREPARATION AND PURIFICATION OF MATERIALS

Hydrogen.—The hydrogen used for the determinations was prepared by the electrolysis of a concentrated solution of barium hydroxide. The form of apparatus used has been described before,[5] and was similar to the one used in the work on chlorine. The water used in the generator was "conductivity water." The barium hydroxide was prepared by recrystallizing the purest commercial compound several times oftener than was necessary to free it of chlorine.[6]

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[4] J. Am. Chem. Soc., **33**, p. 35; 1911.

[5] This Bulletin 4, p. 179; 1908 (Reprint No. 77.). Noyes, J. Am. Chem. Soc., **29**, p. 1721.

[6] It was first attempted to remove any chlorine present by shaking the rather concentrated solution of barium hydroxide with silver oxide. Considerable quantities of silver went into solution, however, and this method was abandoned. It may be well to call attention to the advantages of the barium hydroxide electrolyte at this point. Aside from the fact that it is usually of greater purity than sodium or potassium hydroxides, it offers certain advantages in its manipulation. A solution saturated at about 50° C. was used. On account of the great variation of solubility with the temperature, this deposits a considerable quantity of crystals in the electrolytic cell upon cooling. As the current is sent through the apparatus the solution warms up slightly, some of the crystals redissolve and the resistance goes down. Within certain limits the resistance adjusts itself to the load. Thus in the apparatus used the initial resistance, including a certain outside resistance, was 40 ohms. After the barium hydroxide had dissolved completely the resistance under the same conditions was 10 ohms. The apparatus was connected to a 120-volt lighting circuit and 12 amperes could be sent through the apparatus, giving 0.448 g of hydrogen per hour. The apparatus was kept well cooled by a stream of water when running at this load.

The hydrogen generated in the electrolytic cell passed first through a heated hard glass tube, 40 cm long, filled with platinized quartz. Then it passed through a 30-cm length of fused potassium hydroxide, and then through three tubes, each about 30 cm long, containing resublimed phosphorus pentoxide. The apparatus was of glass throughout, connections between hard and soft glass being made by means of ground joints sealed together by means of a hard cement. When not actually in use the apparatus was sealed up.

Bromine and hydrobromic acid.—In preparing the materials it was desired to limit the reagents used in the process of purification to such as were strictly of the same degree of purity as the material being treated and further to employ such transformations only as would introduce no elements not desired in the final product. While the logic of this plan is obvious, it is not, or can not, always be followed in work of this character. It could not be followed strictly in this work. On the whole the transformations employed in the course of purification of the materials were largely physical. The reagents used in the preparation of the final material were limited as closely as possible to hydrogen, platinum, bromine, potassium salts and water. Aside from these reagents, formic acid was used for the reduction of the bromplatinate to platinum black, and oxalic acid in the form of potassium oxalate. In the case of potassium oxalate two fusions intervened before the final product, potassium bromide, was obtained.

The purification of the bromine and the hydrobromic acid may be considered as one case. The original material was an especially pure sample of bromine.[7]

Thirty-two pounds of this bromine were taken at the beginning of the work. This was distilled three times from a solution of potassium bromide (made from a portion of the same bromine and pure potassium oxalate). It was then cooled until all but a small portion had crystallized. The liquid was rejected. The crystals were allowed to melt gradually and the liquefied bromine was poured off from time to time until half of the bromine had liquefied. The further treatment of this liquefied portion will not be discussed. Although it was treated further in exactly the same way as the crystals from which it had been removed, it did not give so pure a product and was used only in the purification of the platinum. The solid portion melted at −7° C. It was again crystallized and a small liquid residue was rejected. The solid material was again allowed to melt gradually and the melt was removed in small successive portions, in order to wash the crystals remaining as thoroughly as possible, until one-half had been removed. The bromine remaining in the solid condition, which now represented one fourth of the original quantity, melted at −7.2° C. This was designated as D. C. C. and was the only sample that entered into the final work. The liquid quarter which was treated further in a manner similar to the rest was used in the preliminary determinations. It is designated as D. C. L. for convenience.

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[7] The Mallinckrodt Chemical Co. consented to prepare this especially for the purpose. It consisted of about 40 pounds which represented the middle fraction of a large quantity of their purest bromine. The analysis made at the factory according to the method of Andrews showed at the outset a quantity of chlorine which was negligible. Iodine was present in very small quantity. Besides this the chief impurity was a trace of organic material.

The bromine was next converted into hydrobromic acid by means of hydrogen. The hydrogen was generated electrolytically from a solution of pure potassium hydroxide, using four twenty-ampere cells in parallel. From the hydrogen generator the gas bubbled through the heated bromine. The mixture of bromine and hydrogen then passed through a heated glass tube about one meter in length which was filled with platinized quartz (prepared with bromplatinic acid). The hydrobromic acid formed was absorbed by conductivity water. With the proper adjustment of the rate of the hydrogen evolution and the temperature of the bromine, the mixed gases burned as a continuous flame at the entrance to the platinized quartz tube, and neither constituent remained in excess at the end of the system, which was sealed by a water trap. While it was possible to obtain the hydrobromic acid practically colorless it was considered best to carry the reaction on so that a slight excess of bromine remained with the acid.[8] The apparatus was of glass throughout, all connections being made by ground glass joints. The hydrobromic acid thus formed was distilled twice. In the first distillation the excess of water and the free bromine were removed. No iodine could be detected in the advance portion of the distillate. The portion coming over colorless and of the constant boiling concentration was collected. This was then redistilled with some bromplatinic acid[9] made from the same material.

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[8] Some platinum was always found with the acid formed. Whether this was carried over mechanically by the heavy vapor of hydrobromic acid is not certain. The arrangement of the apparatus did not make this seem likely. Wöhler and Spengel, Zs. Anal. Chem., **50** p. 167: 1911, have shown that platinum is volatile when heated in a current of chlorine, less so when heated in a current of bromine.

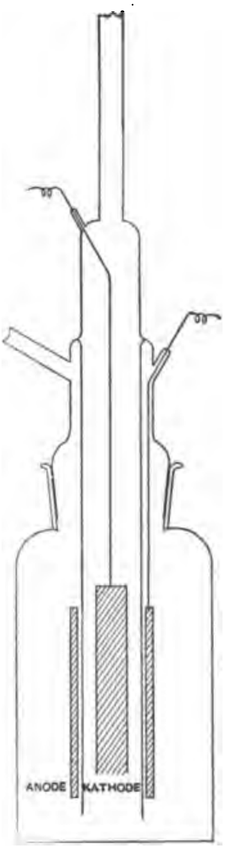

Fig. 1

The hydrobromic acid was then decomposed into hydrogen and bromine by electrolysis. The apparatus is shown in Fig. 1.

The electrodes were of Acheson graphite, the lead wires of silver, and otherwise nothing but glass entered into the composition of the apparatus. When nearly all of the hydrobromic acid had been decomposed the bromine was distilled from the solution. No chlorine could be detected in any of the residues from the distillation.

The bromine so obtained was once more distilled from a solution of potassium bromide made from the same material. One-fourth of this bromine was again converted into hydrobromic acid and then redistilled several times with the addition of water and some bromine, and then with the addition of bromplatinic acid. The first portion of the distillate, containing dilute acid and free bromine, was rejected in every case. The acid was then kept in well seasoned bottles which had been used for the same materials for a long time previously. The remainder of the bromine which was not converted into hydrobromic acid was distilled twice from a solution of HBr and once from bromplatinic acid. The material was then set aside. Directly before use both bromine and hydrobromic acid were distilled at least once in every instance.

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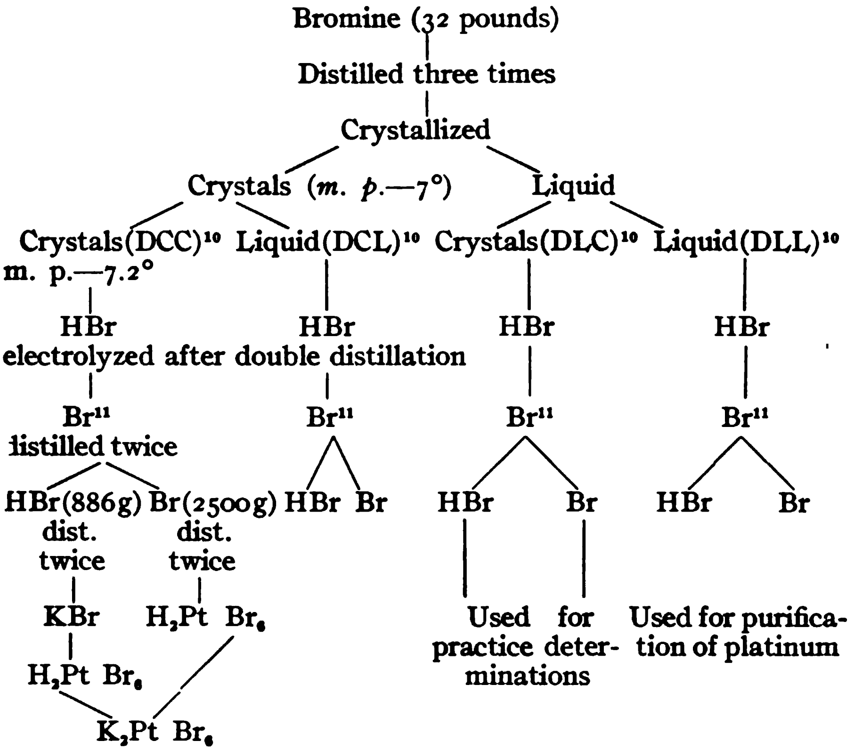
[9] The original bromine contained organic matter. This concentrated largely in the portion which liquefied first and which was rejected. There was not enough of this material obtained to examine it very thoroughly but a substance was found among other things, which gave a bromplatinate. The bromplatinic acid was added to retain this impurity. That aliphatic bromine compounds and cyanogen are at times present in bromine is known.

The following scheme will show at a glance the processes which the material underwent during purification:



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[10] No iodine or chlorine was to be found in any of the fractions. Organic matter in residues from DLL.

[11] No chlorine was to be found in any of the residues from this distillation. For this purpose 20 cc of the mother liquor was neutralized with ammonia and ammonium carbonate added. The bulk of the bromine was then precipitated from this ammoniacal solution by silver nitrate. The solution was decanted after standing over night. Silver was removed by hydrogen sulphide, the solution evaporated with iodic acid and phosphorous acid to remove Br according to the Andrews method. The residue of 3.4 cc gave only the very faintest opalescence with silver nitrate. In connection with the tests for iodine in the materials used, the delicacy of various tests was examined. It was soon found that the presence of the very materials to be tested interfered seriously with the sensitiveness of most of the reactions. As an example of this the characteristic reaction with chloroform was readily obtained with 1 mg of iodine in 20 cc of solution. When 10 cc of constant boiling hydrobromic acid, or the same quantity of saturated potassium bromide solution, were added to the water and test tube was shaken, the coloration of the chloroform vanished. Under similar conditions the palladium iodide reaction failed. The characteristic platinum reaction, used commonly as a test for platinum only, seemed to be affected less than the other tests. In the absence of interfering substances as little as 0.01 mg of iodine would develop the characteristic rose tint in about ten minutes. The most satisfactory method was found to consist in the removal of the salts by fractional precipitation as has been proposed for the examination of water for iodine.

One hundred grams of sodium bicarbonate were neutralized with the hydrobromic acid DLL. To one-half of the solution 1 mg of iodine was added and the two portions were then treated in parallel. About half of the dissolved salt was precipitated by alcohol. The precipitate was boiled and washed with alcohol.

Potassium bromide.—The potassium for the potassium bromide was obtained from the oxalate. The original plan was to prepare the hydroxide by electrolysis of potassium oxalate, using a mercury cathode and a platinum anode. It was necessary to obtain considerable quantities (kilograms) of the hydroxide, and rather large current densities were therefore employed in the trial experiments. The mercury amalgam obtained was decomposed by allowing it to remain in contact with pure water in a large platinum dish. About 500 g of potassium hydroxide were prepared in this way. Upon examination the product was found to contain, besides platinum, considerable quantities of mercury, and the scheme was abandoned.

C. P. potassium oxalate, containing a trace of chlorine only, was recrystallized with centrifugal drainage of the crystals until the ordinary tests failed to show chlorine. Recrystallization was then continued with more rigorous examination of the product. Since a preliminary test showed that silver chloride is appreciably soluble in potassium oxalate solutions, especially when these are rather concentrated, the oxalate was converted into carbonate by ignition. The carbonate was then distilled with pure sulphuric acid and the distillate was examined for chlorine by means of silver nitrate in the nephelometer. After the fifth crystallization the mother liquor contained three parts of chlorine in a million of salt. The material still contained some of the constituents from the glass. Potassium oxalate solutions seems to attack glass especially, and it is not possible to obtain a product which will dissolve to a perfectly clear solution while working in glass. It was therefore necessary finally to recrystallize several times in platinum.

Filtrate and washings were combined, evaporated, and a second precipitation made. After 15 fractional precipitations had been made the mother liquors from the two portions contained respectively 0.93 and 0.91 g of salts. From the portion to which 1 mg iodine had been added 0.5 mg (estimated by colorimetric comparison) was recovered. The sample to which no addition had been made gave no indication of iodine, it is reasonable to assume from this that at this stage of the purification the bromine could not have contained more than 1 : 100 000 iodine.

When liberating small quantities of iodine, less than a milligram for instance, it is a difficult matter to prevent overshooting the mark with the oxidizing agent and consequently setting bromine free. The iodine reaction will naturally not appear under these conditions. This difficulty may readily be circumvented by first adding a ferrous salt, preferably by dissolving some pure iron powder in the acid solution. Dilute bromine water may now be added and as little as 0.2 mg of iodine in 20 cc of solution be discovered, while otherwise a milligram may escape detection.

The potassium bromide used in the purification of the platinum was obtained from this oxalate and purified bromine DCL and DLC. The bromide used in the final determinations was made by converting the oxalate into carbonate by ignition in an electric furnace. This was dissolved and filtered; the solution was neutralized with pure hydrobromic acid, crystallized by evaporation after having been made alkaline, and the salt was then fused in platinum.

Formic acid.—In the reduction of the impure platinum salts in the course of the purification of the platinum, commercial sodium formate was used. For the purer material purified formic acid and potassium carbonate, the latter prepared as for the bromide, were used. The commercial formic acid, which contained some chlorine, was first distilled with silver carbonate. The distillate was chlorine free. It was then fractionally distilled four times and the portions having a density 1.21 to 1.22 were collected. The acid was then recrystallized a number of times and the portion having a melting point of about 8° C was finally used.[12]

Platinum.—Part of the platinum used had been purified for the work on chlorine. About 250 g of platinum were used in all. The platinum was first converted into chlorplatinic acid by aqua regia, the greater part of the iridium being removed by reduction with caustic soda according to Schneider and Seubert.[13] It was precipitated three times as potassium chlorplatinate, the precipitate being reduced in each case with formate and the finely divided platinum black being boiled with dilute hydrochloric acid for some time in order to remove as much of the iron as possible. Next the platinum was converted into bromplatinic acid by means of commercially pure hydrobromic acid and bromine. Some iridium remained insoluble here and was removed by filtration. After the excess bromine had been removed by distillation, potassium bromide was added and the precipitated potassium bromplatinate was collected on a porcelain filter, washed, and then reduced with pure formic acid and potassium carbonate. The finely divided platinum black was heated with hydrobromic acid [14] for seven or eight hours to remove baser metals.

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[12] As is the case with acetic acid, the melting point of formic acid changes much more markedly than the density after the acid has reached a concentration of about 95 per cent. Taking the molecular lowering of the melting point of formic acid as 29° C, 5 per cent of water would lower the melting point about 7.5° C. The further purification was therefore followed by means of the melting point.

[13] Graham-Otto's Lehrbuch II, 4, p. 1153; 1889.

Before being dissolved again the platinum black was finally heated to about 400° C in order to render iridium less soluble and remove volatile products, such possibly as occluded carbon monoxide from the formic acid.

In all, the platinum had been converted into the chlorplatinate three times and into the bromplatinate seven times. The seventh time the bromplatinic acid was prepared by dissolving the platinum electrolytically in hydrobromic acid in an apparatus similar to the one used for the preparation of chlorplatinic acid.[15] During the course of the determinations the platinum was reduced and converted into the bromplatinate three times more. In spite of this long course of purification the platinum was not absolutely free from other platinum metals. (This would, however, not affect the bromine value.) Each time the platinum was dissolved a residue of irridium remained. This was especially noticeable if the platinum had been strongly heated. On the other hand the mother liquor from the bromplatinate always contained platinum metals and traces of iron. It was evident that these residuals were gradually decreasing in quantity. Thus the mother liquor from the last precipitation made, in which 1200 g of bromplatinate were prepared, gave, besides platinum, a few milligrams of other metals consisting mainly of rhodium. Among other things traces of lead could always be detected.

Potassium bromplatinate.—The potassium bromplatinate was prepared by the action of bromine and hydrobromic acid on platinum and precipitation of the bromplatinic acid formed with potassium bromide.

After the platinum black had been washed, dried, and heated to about 400° C it was transferred to 250 cc glass-stoppered bottles. The same bottles had been used in the purification of the platinum and were well seasoned. Seventy to eighty grams of platinum were taken to each bottle. Bromine and hydrobromic acid were then mixed in the ratio $2HBr : 4Br$. Enough of this mixture to combine with all of the platinum and about 30 per cent in excess were then added to the platinum. After waiting a moment and shaking the mixture up a few times, in order to allow occluded gases to escape, the bottles were securely stoppered. They were then placed in beakers containing distilled water and heated on the steambath. After a variable period, depending on the physical condition of the platinum,[16] the metal was completely dissolved.

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[14] The finely divided platinum black always dissolved to a noticeable extent in the hydrobromic acid. This treatment is not particularly well adapted to the removal of baser soluble metals, such as iron. Reprecipitation of the platinum as the complex salt is much more effective. In general the extreme tenacity with which platinum black retains other substances was one of the factors which had to be taken into consideration. With quantities of over 200 g at least 24 hours of continuous washing with hot water was necessary before the wash water was free from bromine. Platinum black thus treated would, nevertheless, give off large quantities of bromine vapors when heated to 300°-400° C. The long-continued washing was necessary to remove formic acid and potassium bromide, which would interfere subsequently in the preparation of the bromplatinic acid.

[15] Weber. Preparation of chlorplatinic acid. This Bulletin, 4, p. 365: 1908 (reprint No. 82). J. Am. Chem. Soc., 30, p. 29.

The solutions of bromplatinic acid from the various bottles were then combined and the excess of bromine was distilled off. After dilution with sufficient water to prevent crystallization the bromplatinic acid was filtered through a platinized Gooch crucible. A small quantity of undissolved material, iridium, usually remained on the filter. The solution was then cooled with ice and added drop by drop to a nearly saturated solution of potassium bromide. An excess of 35 per cent of potassium bromide was used for the precipitation of the bromplatinate. The bromplatinic acid as prepared contained a considerable excess of hydrobromic acid, the potassium bromide was used in excess, and the solutions were kept cold and as concentrated as possible in order to prevent hydrolysis. During the precipitation the material was stirred constantly and was then left standing in the cold solution several hours, with occasional stirring. When freshly precipitated the salt was usually yellow to orange, the color being lighter with the more finely divided precipitate. In course of time the precipitate darkened, usually becoming a beautiful ruby color. The material was not well adapted to centrifugal drainage. It was collected on a Büchner funnel, using S. and S. No. 575 hardened filter paper, washed first with a saturated solution of potassium bromide and then with cold distilled water. It was next dried in a vacuum and then on the steam bath. The bulk of the material was then kept in this condition.

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[16] If the platinum was very finely divided and had not been heated much above 300° C an 80 g lot of the metal would be dissolved completely after 24 hours heating on the steam-bath. At 500° C or so the platinumblack rapidly sinters and becomes gray. The same quantity of this gray sponge requires a week to ten days continuous heating before it is dissolved completely. This marked difference in behavior is worth noting in connection with the attempted separation of the platinum metals by their difference in solubility in various acids or mixtures of acids. At any early stage of purification of the platinum an accident caused considerable loss of time and of some material. A greater quantity of platinum than usual was taken. For this reason the mixture of bromiue, hydrobromic acid and platinum was placed in cracked ice after standing open for a few moments. The bottle was then stoppered. Shortly afterward the material in the bottle commenced to seethe and before anything could be done the bottle burst, throwing the material about with great violence. The platinum used had been prepared some time before and had been set aside in a desiccator. When taken for use it had been moist in this instance. The moisture determination previously made showed 0.65 per cent water. Occluded gases had been given an opportunity to escape while the platinum stood open in the bottle with the bromine mixture. There were no indications of such behavior at any time previous to or subsequent to this single instance. The pressure in the bottles never rose above that due to the vapor tension of the bromine and hydrobromic acid mixture at temperatures near 100° C. Possibly the platinum in this case was in a condition similar to that investigated by Cohen and Strengers, "Explosive Platinum Metals," Zs. f. Phys. Chem., 61, p. 698.

About 200 g of this material were taken for each determination. This quantity of air-dried bromplatinate was transferred to a hard glass tube with ground-glass stoppers and heated to 500° C in an electric furnace. The tube was evacuated to a pressure of 20 mm of mercury, and pure dry air was drawn over the bromplatinate at this pressure. After at least eight hours heating at this temperature the material was transferred, with as little exposure to the air as possible, to the apparatus in which the determination was to be made. The opening through which it had been introduced was immediately sealed off. The apparatus was then evacuated to a few thousandths of a millimeter and heated to 400° C. Any gas which accumulated was removed from time to time. It was then left overnight at about 300° C. Properly prepared and pure bromplatinate would not show an appreciable increase in pressure in the apparatus by the next morning. The changes, if any, amounted only to thousandths of a millimeter. After having been prepared in this way the apparatus containing the bromplatinate was allowed to cool, was cleaned and rinsed with distilled water, and set aside to be weighed. The bromplatinate used in the last five determinations was prepared from hydrobromic acid and potassium bromide, which resulted from the preceding determinations, and from bromine DCC.[17]

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[17] During the purification of the materials, some trial runs were made with bromplatinate prepared from the bromine which has been designated as DLL. This material gave off vapors when heated to 500° C and was in general more unstable than the salt prepared from purer materials. Neither could so good a vacuum be obtained with this salt. On attempting to carry out a determination, a permanent gas was obtained which made it impossible to carry the determination to a satisfactory conclusion. The actual weight of this gas was small and amounted to but a centimeter pressure in a volume of 150 cc, not enough to affect the results. Still it acted as a gas plug and effectually blocked the condensation of the hydrobromic acid formed. Subsequent examination of the platinum salt showed the presence of a small amount of organic matter, which could not be identified with certainty. Organic matter had also been found in the bromine DLL, and none of this material was used in the final determinations.

Water.—The water used was three times distilled. In the third distillation only the middle portion of low conductivity was collected. The final product had a conductivity of 1 to 1.5×10^{-6}. It was kept in a large, glass-stoppered bottle, which was thoroughly aged, and was protected from atmospheric impurities by a soda lime bulb and by a sulphuric acid tube.

Balance and weights.—The balance was a Ruprecht, designed to carry a kilogram in each pan. The manner of drying the air of the balance case has been described in the paper on the atomic weight of hydrogen, by Noyes.[18]

A slight change was made in the housing of the balance case. The balance, with its glass inclosure, was placed in a large copper case, which was blackened inside and out and formed a box which was almost air tight. The whole apparatus was arranged to exclude any radiation while the weighing was being made.[19]

A small window in the case and a lens permitted reading the swings of the balance pointer. A small cardboard funnel, white on the inside and blackened on the outside, illuminated the balance scale without permitting any light to enter the rest of the balance. The metal case itself was grounded, by a wire connection, to the laboratory piping. A small beaker containing radioactive pitchblende was placed inside of the balance case. In this way unequal effects on the balance beam, due to radiations of various kinds, or to electric charges, were eliminated as much as possible.

The three pieces of apparatus, the palladium tube, the platinum tube, and the absorption or hydrobromic acid tube, were weighed against counterpoises of glass. In the case of the palladium tube, by means of which the hydrogen was weighed, the counterpoise was made from the same lot of glass and was shaped as nearly as possible of the same form, in order to duplicate the surface as well as the volume of the palladium tube. Its volume was within 0.15 cc and its weight within 3.5 g of that of the palladium tube. The only vacuum correction necessary on the weight of the hydrogen was that due to these small weights.

The counterpoises for the bromplatinate tube and the hydrobromic acid tube were within a cubic centimeter of the volume of these respective pieces of apparatus. The weights employed here were of necessity larger, since the changes in weight amounted to 80 g and the vacuum corrections were correspondingly larger. It may be noted here in passing that the allowable error on these two pieces of apparatus was eighty times that of the hydrogen tube.

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[18] J. Amer. Chem. Soc., **29**, p. 1723. This Bulletin, 4, p. 179; 1908. (Reprint No. 77).

[19] Manley, Trans. of the Royal Society, 210, p. 387, has shown that small temperature fluctuations of the balance beam, due to radiation, affect the zero of the balance.

Before being weighed all pieces of apparatus were rinsed with distilled water, wiped, and transferred to a glass case through which dry air was passing. Weighings of the hydrogen tube were made after the tube had been suspended in the balance overnight. With the other pieces at least two hours were allowed to elapse between handling and weighing the apparatus. The air current passing through the balance was shut off 15 minutes before a weighing was made. Weighings were made by swings, the sensibility of the balance being determined for each weighing, the readings being taken over a range of 2 mg. The weight taken was the average of four to five observations of about 10 swings each. For the hydrogen, observations were made at separated intervals of time. These individual observations rarely differed by as much as 0.05 mg and usually only by 0.01 or 0.02 mg. With every weighing of the hydrogen tube the zero point of the balance was determined.

The balance and the method of weighing have been described in some detail here for the reason that it seems that the accuracy of the determinations is limited chiefly by the accuracy with which the hydrogen may be weighed. On account of the large ratio small errors on the other constituents practically vanish.

Weights.—The weights used were those which served in the work on chlorine. They were twice calibrated during that investigation and a third time during the investigation on bromine. There was no appreciable change in the corrections.

METHOD OF CARRYING OUT THE DETERMINATIONS

The method of carrying out the determinations and the apparatus used was essentially the same as that used in the chlorine work.[30]

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[30] Loc. cit.

The palladium tube used was capable of absorbing about 2.3 g of hydrogen. The absorption tube for the hydrobromic acid was somewhat larger than in the previous investigation, each bulb having a capacity of about 135 cc. While the theory of the determination was precisely the same as that of the previous work the actual manipulation was considerably more difficult. The first 13 determinations which were made gave results having no value whatever, as far as accuracy is concerned. In some cases the reaction would not proceed with reasonable speed; in others it was not possible to reduce the pressure in the system at the end of a determination. In the latter case it was not possible to find and determine the hydrogen left over, since the hydrobromic acid also present immediately fouled the mercury pump. Another very serious error lay in the accidental diffusion backward of hydrobromic acid to the palladium tube. This acid could be found after the determination had been carried to an end by passing hydrogen over the heated palladium. The hydrobromic acid was given off from the palladium much more slowly and imperfectly than hydrochloric acid under the same conditions.[21]

Considerable time and labor were spent in overcoming these difficulties. The backward diffusion of hydrobromic acid was finally prevented by the use of anhydrous copper sulphate as described further on. The condensation of the hydrobromic acid and its transfer to the water was effected in two operations instead of one. This made it possible to bring the apparatus to a satisfactorily high vacuum at the close of the determination. With these changes in manipulation the large discrepancies between the weight of H + Br and the weight of HBr, which has been usual before, disappeared. On account of these and other apparent errors all determinations made previous to these changes have been disregarded as a whole.

The sketch of the apparatus, Fig. 2, shows the relative arrangement of the parts for a determination. The connection between the hydrogen and the bromplatinate, which at the same time formed the connection to the vacuum pump, contained a section about 5 cm in length which was filled with anhydrous copper sulphate.[22]

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[21] Loc. cit.

After the different parts of the apparatus had been sealed together by means of a hard cement the connections were evacuated to a few thousandths of a millimeter residual pressure. The system was then allowed to stand for 20 minutes, the platinum being heated meanwhile. If no leaks showed the stopcock to the pump was closed and the actual transfer of material was commenced. The condensation bulb for the hydrobromic acid was surrounded by liquid air, and the hydrogen was allowed to enter the bromplatinate tube gradually. The flow of the hydrogen was regulated by the temperature to which the palladium tube was heated and by the adjustment of the stopcocks. The bromplatinate was kept at 250°C during the main part of the determination and raised to 400°C toward the end. The white, solid

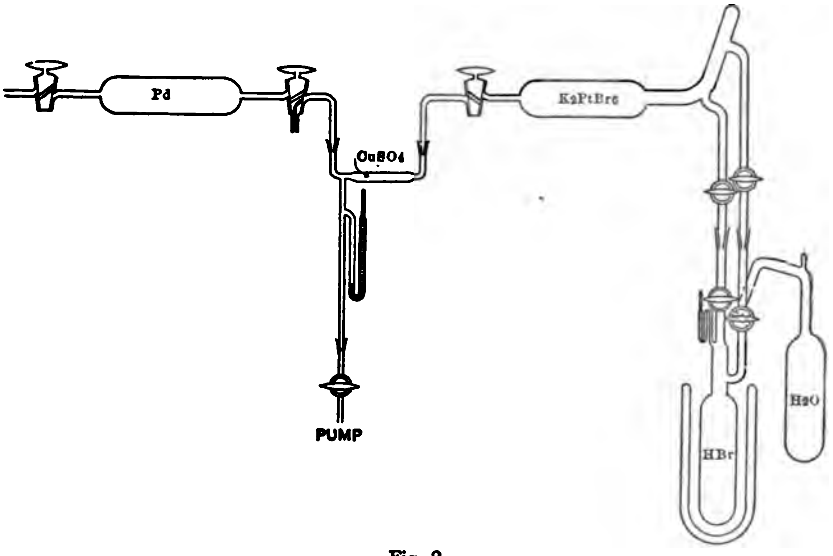

Fig. 2

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[22] The copper sulphate was prepared by recrystallizing the commercial salt until free from halogen. It was then dehydrated, first at low heat, finally adding some sulphuric acid and heating to about 350°C. This material is not affected by hydrogen at normal temperatures and absorbs hydrobromic acid greedily. The salt turns almost black where the hydrobromic acid strikes it. At very low pressures the hydrobromic acid may be liberated by gentle warming, leaving the copper sulphate unaffected. The salt therefore served admirably as an indicator for hydrobromic acid and as a trap to prevent its reaching the palladium tube.

hydrobromic acid appeared in the condensation bulb immediately after the hydrogen was admitted to the bromplatinate. After a while the bulb was filled with a white snowy mass and the condensation became slower, the pressure rising at the same time. From this period onward the process had to be interrupted from time to time in order to allow the hydrobromic acid to melt partially and sinter together into a more compact mass. As the pressure in the apparatus rose considerably during this manipulation it was necessary to close the stopcock between the bromplatinate and the copper sulphate during the process.

When a sufficient amount of hydrobromic acid had been formed, the stopcocks between the platinum and hydrogen tubes were again closed, and the hydrobromic acid formed was condensed as completely as possible. The small amount of hydrogen left in the connecting tube was allowed to enter the platinum tube from time to time as the pressure fell. It usually took two to three hours to reduce the pressure in the apparatus to a small fraction of a millimeter, and the process had to be hastened by alternate warming and chilling of the acid until it had sintered together to a solid block. When the pressure was very low, as was shown by a small manometer sealed on the condensation bulb, the stop cocks between the platinum tube and the hydrobromic acid tube were closed. The liquid air was lowered away from the hydrobromic acid and the pressure was allowed to rise slightly so as to give a constant stream of hydrobromic acid when the connection to the bulb containing the chilled water was opened.[23]

The hydrobromic acid passed over to the water without liquefying, except occasionally at the very end of the transfer. In three hours the 80 g were usually absorbed completely. The platinum tube had meanwhile been kept hot. After a few moments the condensation bulb was again surrounded by liquid air and the stopcocks connecting with the platinum tube were opened. The small amount of hydrobromic acid remaining was now very perfectly condensed in the empty bulb. Any small quantity of hydrogen remaining in the copper sulphate connection was allowed to enter the platinum tube and be converted into hydrobromic acid. Any hydrogen that might have been carried over to the water bulb was allowed to escape by opening the stopcock to this part of the apparatus momentarily from time to time. Any gas coming from here had to pass through the bulb cooled by liquid air, so that water vapor (the liquid was now at —15°C) could not be carried to the platinum. The small amount of hydrobromic acid condensed by this second operation was then transferred to the water.

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[23] After some hydrobromic acid had condensed in the water it was cooled by a freezing mixture instead of by ice alone. For this purpose ice and alcohol were used. This is much more agreeable to work with than either salt or sulphuric acid and ice. One may quite readily attain — 15°C and even lower.

After the determination had been brought to a satisfactory conclusion the apparatus was pumped out by means of the Sprengel pump, as far as the hydrobromic condensation bulb. This latter was examined after it had been weighed. Small traces of hydrobromic acid which had not been condensed did not get into the pump, as they were retained by the copper sulphate. Very often no gases were found on pumping. If there were any they were collected and analyzed, the gas analysis being carried on under reduced pressures. The parts of the apparatus were then allowed to come to normal temperature, taken apart, the cement was carefully cleaned from the connections, the apparatus was rinsed with distilled water, wiped and set aside to weigh. The actual determination required from 12 to 16 hours from beginning to end.

ERRORS AND CORRECTIONS

Hydrogen.—What has been said in the previous paper[24] with regard to the purity of the hydrogen applies to this case. The transfer of hydrobromic acid back to the palladium tube has been prevented by the use of anhydrous copper sulphate. In the ten determinations there was one exception to this. In the tenth determination 1.78 mg of HBr were obtained from the palladium.

Hydrogen was pumped from the apparatus at the end of the first and ninth determinations. The quantities were 0.05 mg and 0.96 mg respectively.

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[24] Loc. cit.

Bromine.—As far as can be seen, the bromine was as pure as could be desired and the bromplatinate was free from volatile impurities. Other halogens were looked for in every step of the process of purification. Volatile constituents were shown to be absent in the bromplatinate as in the case with the chlorplatinate.[25]

An occasional correction was necessary for bromplatinate carried over mechanically to the condensation bulb at the very beginning of the determination. This remained here at the end of the experiment and was removed and weighed after weighing the apparatus. This correction was applied in determinations 6, 8, and 10 and amounted to 155.1, 43.6, and 64.8 mg, respectively.

Hydrobromic Acid.—At the temperatures and under the conditions used there was no evidence whatever of dissociation of the hydrobromic acid, and no free bromine was carried over. The weight of the hydrobromic acid was corrected for the weight of the bromplatinate transferred mechanically, where this was necessary, as is described for the corrections on bromine. A further correction was necessary for the amount of acid absorbed by the copper sulphate. Some hydrobromine acid was found here at the end of every determination. Its amount was determined by titration with N/10th silver nitrate solution. The quantities found were respectively 59.95, 3.30, 8.40, 14.17, 32.28, 4.73, 3.09, 9.32, 6.48, and 61.56 mg.

Agreement Between Weights.—The agreement between the sum of the weights of hydrogen and of the bromine and the weight of the hydrobromic acid served as a final check on the accuracy of manipulation. In the 10 determinations the maximum difference was 2.5 mg. The average difference was 0.26 mg. The sum of the differences for 10 determinations was −2.63 mg. This represents one part in 275 000 on the hydrobromic acid.

RESULTS

The results obtained are given in Table I. The column marked discrepancy gives the differences between H+Br and HBr. The remainder of the table is self-explanatory.

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[25] Loc. cit.

TABLE I

Experiment	Grams H	Grams Br	Grams HBr	Discrepancy in mg	H : Br	H : HBr
1	0.77300	61.28837	62.06052	−0.85	79.2863	80.2853
2	0.86060	68.25033	69.11144	+0.54	79.3055	80.3061
3	0.77607	61.54733	62.32198	−1.42	70.3064	80.3046
4	0.96927	76.88221	77.85135	−0.15	79.3197	80.3195
5	1.07545	85.29562	86.37092	−0.15	79.3114	80.3114
6	0.99689	79.06834	80.06424	−0.99	79.3150	80.3140
7	0.74966	59.45275	60.20500	+2.59	79.3063	80.3097
8	0.98161	77.85554	78.83758	+0.43	79.3141	80.3145
9	1.00131	79.39533	80.39658	−0.06	79.2915	80.2914
10	0.81983	65.02140	65.83867	−2.56	79.3108	80.3077
	9.00369	714.05722	723.05828	−2.63	79.3067	80.3064
					±0.0022	±0.0018
					Combined	
					79.3066	±.0014

In the 10 experiments 9.00369 g of hydrogen were combined with 714.05722 g of bromine and yielded 723.05828 g of hydrobromic acid. The value obtained from these two sums is respectively 79.307 (1) and 80.306 (9).

The final ratio obtained from these figures for H : Br is 79.306 (7), with a probable error of 0.0022. The ratio found from H : HBr is 80.306 (4), with a probable error of 0.0018. Combining the two the value is 79.306 (6) ± 0.0014. The numerical value of the probable error is somewhat larger than that of the chlorine ratio obtained in a similar manner. Relatively it is approximately the same or even somewhat smaller.

In connection with this determination of the bromine : hydrogen ratio, it may be of interest to note the relation of this value to the value determined for chlorine previously.

Richards and Müller[26] obtained a ratio between bromine and chlorine equal to 0.44369, while Baxter[27] obtained 0.44367, for the same ratio. Combining the average of these two ratios, 0.44368 with the value here obtained for bromine we get 79.3066 × 0.44368=35.186(7) for the hydrogen : chlorine ratio. The value obtained by Noyes and Weber was 35,184. Dixon and Edgar obtained 35,195[28] and Edgar in the second series obtained 35.193[29]

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[26] Richards. Atomgenichte p. 825 (1909).

[27] Loc. cit.

Taking the atomic weight of hydrogen[30] as 1.00779, the value for bromine on the oxygen basis becomes 79.924, as against the value 79.920 given by the International Commission for 1912.

WASHINGTON, November 1, 1912.

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[28] Phil. Trans. 205A. p. 169 (1909).

[29] Proc. Roy. Soc., 81A. p. 216 (1908).

[30] Clarke: Recalculation of Atomic Weights, p. 41, 1910.

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I. BRIEF HISTORY OF INVESTIGATIONS ON THE SILVER VOLTAMETER

The earliest employment of electrochemical decomposition as a means for the measurement of electricity appears to have been by Gay Lussac and Thénard[1] about 1811. They arranged a gas voltameter that gave them a qualitative idea of the conductivity of various solutions and the strength of their battery. It remained, however, for Faraday[2] to enunciate the conditions on which it may be used for the exact measurement of electric current. He, too, used a gas voltameter which he declared to be the "only actual measurer of voltaic electricity which we at present possess." Because of this he named it the volta-electrometer. He suggested the possibility of using a voltameter in which a metal should be deposited to measure the current, but he does not appear to have done it himself. The silver voltameter appears to have been first used by Poggendorff[3] and described by him in a footnote. He was attempting to find the minimum current that would cause a visible decomposition of water. His cell consisted of two platinum plates in a saturated solution of Ag_2O in HNO_3. After several hours a silver deposit was visible, without any of the water in his water voltameter having been decomposed. He raised the interesting question as to why the silver deposit is discontinuous, and whether any of the current passed through the platinum surface on which there was no silver deposited. An illustration of this voltameter appeared later.[4]

Sixty or more papers have been published dealing with the silver voltameter. In a part of these papers the authors have been primarily concerned with an investigation of the instrument as a means of measuring current; in other cases the investigators have used the voltameter merely to measure current, using the electrochemical equivalent determined by other observers; while a third class of papers is devoted to a study of various problems of electrolysis. Of this last class one of the earliest is by Almeida.[5] He used the silver voltameter to study the decomposition of a simple salt and the effect of acid. He concluded that if both acid and salt are present they are both decomposed, but part of the metal deposited is due to a secondary reaction of the nascent hydrogen, and if acid is not present in excess before the electrolysis begins it will be formed to some extent as soon as the current starts, even with a soluble anode.

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[1] Recherches Physico-Chimique, 1, p. 12; 1811.

[2] Experimental Researches, 1, p. 217; 1834.

[3] Pogg. Ann., 70, p. 181; 1847. (We are indebted to Prof. R. H. Weber of Rostock for this reference.)

[4] Wiedemann's Galvanismus, 1st ed., 1, p. 314; 1861.

Kohlrausch[6] advised the use of silver in the voltameter. He used a silver crucible as cathode with a 15 per cent solution of $AgNO_3$ and the silver anode wrapped in cloth. A few years later Kirmis,[7] working at the University of Berlin under Helmholtz, employed the silver voltameter to measure electric current, and, becoming interested in the various forms of silver deposit, made a very careful study of them. We shall refer at length to his paper later on, in connection with the striations of silver deposits.

The first absolute measurement of the electrochemical equivalent of silver to be published was by Mascart,[8] who concluded that the silver and copper voltameters were more reliable than the gas voltameters. He used two plates for his electrodes and derived his values from the loss at the anode as well as the gain at the cathode. His value for the electrochemical equivalent, which was later corrected[9] to 1.1156 mg per coulomb, was obtained with the aid of a current balance. In 1884 Carhart[10] made use of the silver voltameter to measure the voltage of a Daniell cell, a principle which constitutes the chief use of the voltameter to-day, in connection with the cadmium cell.

The first thoroughly systematic study of the silver voltameter was by Lord Rayleigh and Mrs. Sedgwick.[11] They used platinum basins of considerable size for the cathodes and sheet silver anodes wrapped in filter paper, a form which has been much used since, and named after Lord Rayleigh. The possibility of errors arising in this form has been a subject of lively discussion by many observers for the last 20 years. Most investigators have attributed the trouble to complications arising at the anode, which were supposed to cause an excess of silver to be deposited on the cathode, if the latter is not suitably protected. A large part of our work has been devoted to a further investigation of this question, and we shall show that this effect is due not to the filter paper being an imperfect separator of the anode and cathode solutions, but to its not being chemically inert. Lord Rayleigh and Mrs. Sedgwick found an excess deposit when silver acetate was added to the solution and they at first attributed this to inclusions of the mother liquor, but later to the acetate itself.

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[5] Ann. de Chim. et Phys. Series III, **51**, p. 257; 1857.

[6] Pogg. Ann., **140**, p. 170; 1873.

[7] Pogg. Ann., **158**, p. 121; 1876.

[8] J. de Phys. Series II, **1**, p. 109; 1882.

[9] J. de Phys. Series II, **3**, p. 283; 1884.

[10] Am. J. Sci., **28**, p. 374; 1884.

[11] Phil. Trans. A, **175**, p. 411; 1884.

They analyzed their deposits for inclusions, but without conclusive results. They, however, adopted the weighings after "strong heating" of the deposits for their final results. Their value for the absolute electrochemical equivalent in terms of their current balance was 1.11794 mg per coulomb. A very important fact in this work is that they obtained heavier deposits by about 2 in 10 000 in large bowls than in the smaller ones. Schuster and Crossley (see p. 155) attempted to explain this as due to the difference in size of the anodes used in the large and small bowls, but, as will be shown in the third paper of this series, it was due to the contamination of the electrolyte by the filter paper.

Shortly after this work another very important paper by F. and W. Kohlrausch[12] was published, although the work had been begun before that of Lord Rayleigh. It is largely taken up with a discussion of their tangent galvanometers for making an absolute determination of the current.

They used a platinum cup with silver anode protected by a small glass dish underneath as one form, a siphon voltameter as another, while a third form consisted of two parallel plates standing in a beaker, the cathode being protected from loss of silver particles by a small semicircular glass dish. The electrolyte was made from fused silver nitrate. They give as their final result 1.1183 mg per coulomb. All of their voltameters were very small.

Two papers quickly followed in which the voltameter was used as a measurer of current for the determination of electromagnetic rotation constants, basing the results on the work of Lord Rayleigh and F. and W. Kohlrausch. These were by Arons[13] and

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[12] Wied. Ann., 27, p. 1; 1886.

[13] Ann. d. Phys., 24, p. 161; 1885.

Koepsel.[14] The latter subsequently published[15] an absolute determination of the electrochemical equivalent, using a Helmholtz balance and obtaining 1.11740 mg per coulomb.

Thomas Gray[16] made an extended study of the silver and copper voltameters for the purpose of standardizing electrical measuring instruments. He preferred vertical plates in a beaker to the more usual forms and like Mascart used the loss at the anode to check the gain at the cathode. His conclusions were unlike those of his predecessors or successors in recommending very small current densities and weak solutions, and that the anodes should be larger than the cathodes to avoid slime. He made a few determinations of the electrochemical equivalent using a sine galvanometer obtaining 1.1183, but he does not consider this reliable owing to errors in the galvanometer.

Potier and Pellat[17] made an absolute measurement of the electrochemical equivalent in terms of an electrodynamometer using a Clark cell as an intermediary standard. Their attention was chiefly devoted to the measurement of current rather than the errors arising in the voltameter, which they used only twice, and hence little weight can be attached to their very high value of 1.1192 mg per coulomb.

Schuster and Crossley[18] attributed the excess weight of deposit in the large bowls over that in the smaller ones as found by Lord Rayleigh to the difference in size of the anodes, but it must be noted that in suspending the silver by platinum wire they had in reality a combination silver and platinum anode. Their observations showed that some of the current left the platinum wire, which was likely to produce marked changes in the acidity of the solution and vitiate the results. Their deposits made in vacuo were one part in two or three thousand heavier than in free air, which they attributed to the absence of oxygen. They apparently used the same solution repeatedly in the filter paper voltameter and thereby lessened to a considerable extent the value of their work.

Glazebrook and Skinner[19] in a determination of the emf of the Clark cell used the silver voltameter, following the procedure of

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[14] Ann. d. Phys., **26**, p. 476; 1885.

[15] Ann. d. Phys., **31**, p. 250; 1887.

[16] Phil. Mag., **22**, p. 389; 1886.

[17] J. de Phys., **9**, p. 381; 1890.

[18] Proc. Roy. Soc., **50**, p. 344; 1892.

[19] Phil. Trans., **183** A, p. 567; 1892.

Lord Rayleigh. Assuming the value 1.118, they found 1.434 as the value for the cell. The differences among the voltameter determinations, even in the same run were large, and they attribute them to the rate of deposition of the metal. Kahle[20] working on the same problem, however, made some study of the behavior of the voltameter, finding deposits heavier by 5 in 10 000 when the solutions were rendered basic by boiling a part of the $AgNO_3$ for a long time with Ag_2O. Deposits made in vacuo were 4 parts in 10 000 heavier than those made in air. In using the voltameter under such conditions to measure current, he increased the value for the electrochemical equivalent by these amounts.

Novak,[21] while not the first to ascribe the errors of the voltameter to effects at the anode, appears to have been the first to suggest the formation of the complex ion at the anode. The same idea was probably independently put forward by Rodger and Watson,[22] who found a continued increase in the deposit resulting from successive use of the same electrolyte.

A paper by Behn[23] on the striated arrangement of galvanic deposits is of especial interest, because of his many ingenious experiments to determine their cause. We shall refer at length to this paper later on.

A study of the effect of dissolved gases in the voltameter was made by Myers.[24] He reports a decrease in deposit in an atmosphere of CO_2, a result not since confirmed. His paper contains only the results of observations without any attempt at theoretical explanation.

Two interesting determinations of the emf of the Clark cell followed, the first by Kahle,[25] who found that the increased deposits due to the successive electrolysis of the same electrolyte were due (1) to the supposed fact that more silver is deposited upon a previous deposit of silver than upon a clean platinum surface and (2) to some change arising in the electrolyte. His results for the emf of the Clark cell at 15° were:

1.4327 from new electrolyte,
1.4341 from used electrolyte.

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[20] B. A. Report for 1892, p. 148.

[21] Proc. Roy. Bohem. Ac. Sci. Prague, 1, p. 387; 1892.

[22] Phil. Trans., 186 A, p. 631; 1895.

[23] Wied. Ann., 51, p. 105; 1894.

[24] Wied. Ann., 55, p. 288; 1895.

[25] Zs. f. Instrk., 17, p. 145; 1897.

The change occurring in the electrolyte in a filter paper voltameter due to repeated use we shall discuss later. The second paper on this same subject was a carefully executed piece of work by Perot and Fabry.[26] They followed closely the specifications of the Chicago congress and found 1.4341 volts for the Clark cell at 15°. They had previously determined the voltage in absolute units and from the ratio obtained a value for "*v*" in very close agreement with the determination made recently at the Bureau of Standards.[27]

Kahle[28] in 1899 published the results of an extended investigation of the silver voltameter, using as a reference standard several Clark cells. His voltameters were similar to the platinum cup voltameters of Kohlrausch, but considerably larger. He tabulated in all 115 deposits, noticing that many of them were striated, which he found to be characteristic when the same solution is used several times. In some cases he found a liberation of acid which he concluded accompanied the formation of oxidation products at the anode. He found the electrochemical equivalent to be 1.1183 mg per coulomb.

Patterson and Guthe[29] made an absolute determination of the electrochemical equivalent, using an absolute electrodynamometer. They used the filter paper form of voltameter and added Ag_2O to insure the neutrality of the electrolyte, which probably accounts, in part at least, for the high value, 1.1192 mg per coulomb, which they obtained.

This work was followed by papers by Richards, Collins, and Heimrod, and by Richards and Heimrod.[30] These papers had a marked effect on much of the work that followed. They undertook to find the cause of the difference between the atomic weight of copper as determined electrolytically and chemically. This led to an extended investigation of various forms of the voltameter, from which they derived corrections that brought the work of previous observers into closer agreement. From these corrected values they derived the electrochemical equivalent of silver, obtaining 1.1175 mg per coulomb. In the first of these papers the authors definitely stated that the filter paper voltameter was in error because a complex ion was formed at the anode and passed through the filter paper and deposited an excess of silver on the cathode. To obviate this they substituted a porous cup of porcelain for the filter paper which was supposed to serve as a more perfect separator between anode and cathode. This form of voltameter has since been much used under the name of the Richards or porous pot voltameter.

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[26] Ann. de fac. Sci. Marsaille, 8, p. 201; 1898.

[27] This Bulletin, 3, p. 433; 1907.

[28] Ann. d. Phys., 67, p. 1; 1899.

[29] Phys. Rev., 8; Dec., 1898.

[30] Proc. Am. Acad. Sci., 35, p. 123; 1899. Proc. Am. Acad. Sci., 37, p. 415; 1902.

We have found it to give excellent service, although our reason for using it has been very different from that given by Richards. The principal reason given by Richards and Heimrod for believing in the existence of the heavy anode ion is that under certain circumstances silver was found to be deposited on silver from an anode solution without an electric current. This observation was not confirmed by Smith, Mather, and Lowry, although still insisted upon by Richards[31] in 1908. Neither have we been able to confirm this observation of Richards, but we have found that a solution contaminated with filter paper will cause an increase[32] in the weight of silver immersed in it regardless of whether this solution had been in contact with the anode or not. We shall discuss the question of filter paper versus porous pot voltameter fully in a later paper. Richards determined the inclusions in his deposits of silver by heating them over an alcohol flame and found a loss in weight of 0.02 per cent, even in deposits from his purest electrolyte.

Merrill,[33] working at Johns Hopkins, carried out a series of measurements on the effect of pressures (above atmospheric), temperature, used solutions, size of anodes and comparison of the filter paper form with a voltameter without septum. His results were negative, except in the case of used solutions which gave a heavier deposit. This effect he attributed to a reduction in valence of the silver ion.

Leduc,[34] reporting to the International Congress of Physics, reviewed the voltameter situation and advocated the adoption of 1.119 instead of 1.118 for the electrochemical equivalent. In later papers[35] he continued his discussion of the effect of impurities present in the electrolyte particularly with reference to HNO_3 and AgOH. His studies led him to the conclusion that the anode current density should be very small in order that only the simple reaction $Ag + NO_3 = AgNO_3$ may occur. With higher current densities the formation of acid occurs. The $AgNO_3$ and HNO_3 are then electrolyzed together, the H going to the cathode and reacting to form ammonia salts and the precipitation of silver. He believed that the presence of AgOH in solution is not objectionable *provided it is in solution.* In some of our latest experiments, to be described in the subsequent papers, we have found this so, but the AgOH is often present in a colloidal condition and may cause very serious errors. He advocated the use of Ag_2O to neutralize the acid of the electrolyte. In testing the acidity he notes the necessity of precipitating the silver before making the tests with methyl orange. This, we think, had not been mentioned before, and for this reason Leduc's acid determinations should have much greater weight than others previously made. Leduc thought that there is always an equilibrium value of the acid, and on this basis sought to reconcile the differences between Kahle and Patterson and Guthe. His experiments showed that the baser metals produce relatively little effect if present. With Pellat[36] he made an absolute determination of the electrochemical equivalent, using Pellat's electrodynamometer. The mean value was about 1.1195. These high values must be ascribed, in part at least, to the large amount of filter paper and muslin present for a long time in the voltameter. It may be in part due to an error in the measurement of current, which might also account for the high value obtained by Potier and Pellat (loc. cit.).

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[31] Proc. Am. Ac. Sci., 44, p. 91; 1908.

[32] Second Paper of this Series by Rosa, Vinal, and McDaniel.

[33] Phys. Rev., 10, p. 167; 1900.

[34] Rapp. Cong. Int. de Phys., 2, p. 440; 1900.

Watson,[37] in a paper dealing with the earth's magnetic field, gives much of importance concerning the previous work on the voltameter. He used both the porous cup and filter paper form, preferring the latter. He adopted the value 1.118 mg per coulomb, and expressed his results in terms of the cadmium cell at 20° and the filter paper voltameter.

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[35] J. de Phys., Series IV, **1**, p. 561; 1902. Comptes Rendus, **135**, pp. 23, 237, 395; 1902.

[36] Comptes Rendus, **136**, p. 1649; 1903.

[37] Phil. Trans. Vol. A, **198**, p. 431; 1902.

Two other papers appeared during 1902, the first being a short one by Mylius,[38] in which he dealt with the chemistry of the voltameter. Among other things he noted that the organic parts of the filter paper can act upon the $AgNO_3$ and produce a red silver precipitate, but this warning seems to have escaped general notice. The other paper is by Farrup,[39] who worked with cyanide solutions.

Guthe,[40] working at the Bureau of Standards, used (1) filter paper form, (2) the Ag_2O form, (3) the porous pot form, (4) the large anode form, (5) Leduc's form. He noted the agreement of (3) and (4), which is not surprising since they were practically the same voltameter. He regarded his work as furnishing further evidence that the complex ion was the source of trouble. In his later work he sought other means of eliminating the complex ion, believing the porous cup was not sufficient protection. In terms of his work on the Gray absolute electrodynamometer he gave the electrochemical equivalent of silver as

1.11773 mg per coulomb

as determined by the porous cup type.

Van Dijk and Kunst[41] attributed the differences among previous observers both to the measurement of current and to the handling of the voltameters. They employed two tangent galvanometers and made determinations using two filter paper voltameters. They relied on the reproducibility of the voltameters and the agreement of results of the two galvanometers to prove the accuracy of their measurements. Their mean value is 1.11823 mg per coulomb.

Snowden[42] investigated the possibility of getting a smooth deposit from $AgNO_3$. By adding glue to the $AgNO_3$ he obtained some purple colloidal deposits.

Van Dijk[43] made a careful comparison of the filter paper and porous cup form and found 0.023 per cent as the difference. A siphon voltameter gave a little heavier deposit than the porous pot form, for which fact he could not account, but he concluded that both gave lower values than the filter paper form, because in both the anode solution was kept away from the cathode. In discussing used solutions, he ascribed the excess of deposit as due in part to the complex ion and in part to the extracted dextrine products from the filter paper. He carried out tests [44] designed to expel the foreign matter included in the deposits by heating them to redness, but his results showed no appreciable change in weight. He gave as the value for the electrochemical equivalent of silver in absolute measure 1.1180 mg per coulomb.

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[38] Zs. f. Instrk., **22**, p. 155; 1902.

[39] Zs. f. Electro-Chem., **8**, 569; 1902.

[40] This Bulletin, **1**, p. 21; 1904. Phys. Rev., **19**, p. 138; 1904. Phys. Rev., **18**, p. 445; 1904. This Bulletin, **1**, p. 349, and **2**, p. 33; 1906.

[41] Ann. d. Phys., **14**, p. 569; 1904.

[42] J. Phys. Chem., **9**, p. 392; 1905.

[43] Ann. d. Phys., **19**, p. 249; 1906. Arch. Neerland. des Sci., Series II, **9**, p. 442.

Carhart, Willard and Henderson [45] published a preliminary paper on the use of silver perchlorate as an electrolyte for the silver voltameter, claiming as advantages in its use an adherent deposit and freedom from reduction products. They report, however, that the deposits were generally striated and heavier than the deposits from the nitrate, which is, of course, sufficient evidence to condemn its use.

Duschak and Hulett [46] published the results of a careful investigation of the voltameter in which they attained a high degree of reproducibility, using the porous pot form. In vacuo and in nitrogen they got slightly smaller deposits than in free air. In attempting to explain this they analyzed their silver deposits by heating a portion in a closed tube and examining for gas and liquid. They found the inclusions to be about 0.011 per cent in free air and slightly smaller in vacuo, which partly explains the observed difference in deposits.

The first of the recent series of determinations by the national laboratories was published by Smith, Mather and Lowry in 1907.[47] Their determination of the electrochemical equivalent of silver, 1.11827 mg per coulomb, is in terms of an absolute current balance and using several forms of voltameter. This elaborate and comprehensive paper is discussed on pages 167, 205 and also later in these papers.

In 1908 the careful work of Jaeger and von Steinwehr [48] of the Reichsanstalt was published. They give a detailed account of the precautions taken in their work, particularly in the matter of weighing the deposits. Using 1.118 mg as the electrochemical equivalent they determined the voltage of two sets of cadmium cells, old and new, using a porous cup voltameter and another without septum. They prefer the latter and give 1.01834 volts at 20° as the value of their new cells. The difference at first apparent between the two forms of voltameter vanished when experiments were made using them in series and they concluded that the forms are in good agreement.

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[44] Arch. Neerland. des Sci., Series II, **10**, p. 277.

[45] Trans. Am. El. Ch. Soc., **9**, p. 375; 1906.

[46] Trans. Am. El. Ch. Soc., **12**, p. 257; 1907.

[47] Col. Researches N. P. L., **4**, p. 125.

[48] Zs. f. Instrk., **28**, pp. 327, 353; 1908.

Janet, Laporte, and de la Gorce[49] working at the Laboratoire Central d' Electricité, determined the voltage of the Weston cell by an absolute current balance and from the value thus found obtained 1.11821 as the electrochemical equivalent of silver using the filter paper form. An error was subsequently discovered[50] that lowered their value for the standard cell by about 3 in 10 000 which would considerably increase their value for the electrochemical equivalent. In a subsequent series of experiments[51] using the English values of their resistances and standard cells they obtained values very concordant with Smith, Mather, and Lowry.

Kohlrausch and Weber[52] pointed out that if a temperature coefficient for the voltameter such as was found by Lord Rayleigh and others really existed it would introduce great complications in theoretical chemistry. They tested the matter by examining for a deposition of ions at a surface bounding two widely different temperatures in a tube containing one of several salts in water thickened with arrow root. Their results showed that there was no change in the electrochemical equivalent as great as 1 in 10^7 per degree.

Since Richards had used his own work to assign corrections to other determinations, and among them that of F. and W. Kohlrausch based on the effect of anode liquid, F. Kohlrausch[53] undertook a recomparison of one of their original voltameters with forms in which the anode liquid was more confined. The difference found was only 2 in 100 000 and he therefore concluded that their earlier determination was correct.

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[49] Bul. Soc. Int. Electr., 8, p. 523; 1908.

[50] Comptes Rendus 153, p. 178; 1911.

[51] Bul. Soc. Int. Electr. 10, p. 157; 1910.

[52] Ann. d. Physik., 26, p. 409; 1908.

[53] Ann. d. Phys., 26, p. 580, 1908.

Bose and Conrat[54] published a brief paper on a silver microvoltameter, but this instrument is not suitable for the work we have in hand.

Eisenreich[55] published a paper supporting the complex ion theory of Richards. It does not appear from the data that he gives that the purity of his solutions was sufficiently high. We have observed many of the phenomena that he gives as establishing the existence of the complex ion and have found that they do not occur when solutions of a high degree of purity are used. Since 1909 we have used potassium permanganate[32] in testing $AgNO_3$ for reducing impurities and colloidal silver, and our results have been communicated to the various national laboratories and to the American Physical Society, but have not been hitherto published except in abstracts.

The work contained in the present paper was in a measure preliminary to the work of the International Technical Committee whose report has just been published. We shall not, therefore, attempt to review that work here. There still remain a few papers bearing on the voltameter indirectly, but it is impossible for us to deal with these.

Recent work in this and other laboratories has shown that impurities in the electrolyte produce such widely differing effects depending on the amount and size of the voltameter and the acidity or alkalinity of the electrolyte that we do not think it advisable to tabulate the preceding results and apply hypothetical corrections in order to obtain a value for the electrochemical equivalent. These papers contain many things of interest which it is impossible to discuss owing to lack of space. But the absolute values found and the differences between the various forms of voltameters were so much affected by impurities in the electrolyte used, that it is impossible to apply corrections or to attach much importance to the numerical results. We consider that the work of the International Technical Committee beginning in April, 1910, marks an epoch in the work on the voltameter, because electrolytes known definitely to conform to a sufficient standard of purity were used, and the close agreement of the porous pot and no-septum forms of voltameters was established.

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[54] Zs. f. Electrochemie, 14, p. 86; 1908.

[55] Zs. Phys. Chem., 76, p. 643, 1911.

II. INTRODUCTION AND OUTLINE OF WORK

The silver voltameter was chosen as the official primary standard for the measurement of current by the International Electrical Congress at Chicago in 1893, the ohm being fixed by the resistance of a specified column of mercury and the volt by the emf of the Clark standard cell. At the International Electrical Conference of 1908, at London, two instead of three primary standards were chosen, namely, the ohm and the ampere. These were specified as before in terms of the resistance of a column of mercury and the current that will deposit a given mass of silver per second, respectively, the volt being defined in terms of the ohm and ampere by means of Ohm's law. But the numerical value to be assigned to the Weston Normal Cell, which was chosen at London in place of the Clark cell as the instrument for expressing concretely the value of the international volt, would depend upon the specifications adopted for the mercury ohm and the silver voltameter. It was therefore important that the specifications adopted for these two primary standards should be such as to give a very high degree of reproducibility, the more so since the accuracy obtained in absolute measurements has increased considerably in recent years, and the precision demanded in the standardization of instruments is also much higher than formerly.

Up to the time of the London Conference many papers had been published dealing with the silver voltameter (or coulometer), and of these several had given the results obtained using both the Rayleigh and the Richards voltameters.[56] In every case but one, the Rayleigh form, in which filter paper is used, had been found to yield a heavier deposit of silver than the Richards form. The difference was not uniform, varying generally from 4 to 5 parts in 10 000. The theory given by Richards to explain this difference was generally accepted. However, in an extended investigation of various forms of voltameters published in 1907, Smith, Mather, and Lowry reported agreement between these two forms, and believed the filter paper voltameter, as they used it, to be a reliable instrument, and the value given by it to be normal. It was at this point in the history of the voltameter that the work described in this paper was taken up (1908).

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[56] The name "coulometer" was suggested by Prof. T. W. Richards, as more appropriate than voltameter, since the instrument measures coulombs, and the word voltameter may be confused with voltmeter. "Coulometer" has been used by several authors, and is preferred at the Bureau of Standards. However, in deference to the decision of the London conference, which considered the question and decided to adhere to the old name, we use the name voltameter throughout these papers.

The investigation of the silver voltameter at this bureau was first begun, however, in January, 1904, by Dr. K. E. Guthe, and the results of his work were published in November of the same year. He found as the value of the electrochemical equivalent of silver using the porous cup or Richards form of voltameter 1.11683 mg per coulomb [57] and for the filter paper or Rayleigh form 1.11736, in terms of the Clark cell taken at 1.434 volts and the international ohm. The former of these values he subsequently changed to 1.11773 on the basis of his absolute measurements of the voltage of Clark and Weston standard cells by means of an electrodynamometer.[58] We have endeavored to connect our present work with these early values of Dr. Guthe and find that assigning the same numerical values to the standard cells that our values are about 2 parts in 10 000 larger than his, a closer agreement than could be expected when one considers the many sources of difference between that work and the present.

Nothing further was done with the silver voltameter at the Bureau of Standards until June, 1907, when Dr. N. E. Dorsey with the assistance of the present authors began what was intended to be a short series of determinations to accompany the absolute measurements of current with the Rayleigh balance which was then under construction, and to attempt to confirm the work recently done at the National Physical Laboratory. Some additional equipment was purchased and some refinements in the weighings of the platinum dishes were made. The differences between the individual determinations, however, were larger than was expected and larger than could be justified on the ground of accidental errors. Because of this and the fact that only the filter paper voltameter was used, the results obtained are of little value now, but it is interesting to observe that with new solutions of silver nitrate the mean value found was 1.11746 mg per coulomb (taking the Weston cell as 1.01890 at 25° C), which agrees closely with the mean obtained in the present work [59] with the same type of voltameter. With used solutions a mean value of 1.11761 was found, being 14 parts in 100 000 higher than from the unused solutions. This increase had been noted by many investigators before, but we believe that no satisfactory explanation has as yet been offered for it. We have confirmed this result and in the later papers of this series a theory will be offered to explain it which we believe will be found adequate. Dr. Dorsey's work, which has not been published, was brought to a close in September, 1907.

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[57] This Bulletin, 1, pp. 21 and 349.

[58] This Bulletin, 2, p. 33.

[59] This paper, p. 196.

In July of the following year more extensive preparations for voltameter work were begun by the present authors. Two new balances for weighing the deposit were bought and installed in a special constant temperature room in order to increase the precision of weighing. Selected standard cells maintained in an oil bath at uniform temperature, together with other additions of apparatus increased the facilities for accurate work. Some preliminary deposits without the measurement of current were made as manipulation tests.

On October 8, 1908, the first series of quantitative experiments was begun. We used at first only the filter paper voltameter, and obtained a fair degree of reproducibility, but the difference between it and the porous cup form of voltameter which developed on using the latter for the first time in December, 1908, led us into an investigation of the effect of filter paper.

In the extended investigation of the silver voltameter by Smith, Mather, and Lowry,[60] published in 1907, they compared the filter paper form with the porous cup form and found, contrary to the experience of many other observers, that the weight of silver deposited in the two forms agreed very closely. They had treated the porous cups differently in one important respect from what anyone else had done, namely, baking them in a furnace at a high temperature after washing with acid. They attributed the agreement between the two forms in part, at least, to this special treatment, which they believed freed the porous cups more perfectly from acid than had been done before. They believed therefore that, as they used them, both forms of voltameters gave normal deposits, which were determined with great care, and by means of which, together with an absolute current balance, the electrochemical equivalent of silver was ascertained to be 1.11827 mg per coulomb.

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[60] Col. Researches N. P. L., 4, p. 123.

We found, however, that the filter paper form gave consistently heavier deposits than the porous cup voltameter, and that the deposits were imperfectly crystalline and distinctly striated. Using two or three sheets of filter paper increased the difference between the two forms to two or three times its value when a single sheet was used, and wrapping a sheet of filter paper around the porous cup gave the deposit the characteristic striated appearance and heavier weight of the ordinary filter paper voltameter.

It thus became evident that the filter paper employed in the voltameter was a source of serious disturbance, and that the usual explanation of the difference between the two forms of voltameter was incorrect. Instead of the porous cup serving to protect the cathode from secondary products formed at the anode, and the filter paper voltameter giving a heavier deposit because it was a less efficient septum than the porous cup, it became evident that the filter paper itself was the source of important chemical action in the electrolyte, while the porous cup on the other hand was neutral and did not so contaminate the electrolyte. At this point in the investigation Dr. A. S. McDaniel joined us to study the chemical questions that had arisen, and first of all to learn what the action of filter paper is whereby so considerable a change is made in the appearance and weight of the deposited silver. The work done subsequent to this time will be described in three papers following this, and in these papers Dr. McDaniel will appear as joint author. A long series of experiments was also made to find the effect of other organic substances, such as cotton, linen, and silk fabrics, various kinds of paper and wood fiber, etc. These were followed by chemical investigations to ascertain the nature and explanation of the various phenomena observed. This work will be fully discussed in the second paper of this series. Our explanation of the reason why Smith, Mather, and Lowry found the porous cup form of voltameter to give as heavy a deposit of silver as the filter paper form is given fully in the fourth paper. Briefly it is, that baking the porous cups to free them from acid renders them appreciably alkaline and this we have found increases the deposit. By chance, this increase of weight we suppose was substantially the same as the increase in the Rayleigh form produced by the filter paper.

We also gave considerable attention to the explanation of striations. It has long been known that under certain circumstances the silver deposited in a voltameter is strongly striated. Sometimes it is slightly striated and sometimes it is altogether free from striations. This subject had been studied by several investigators, but no satisfactory explanation had been offered. In the second paper an account of studies of this subject and an explanation which appears satisfactory will be given.

Having discarded filter paper from the voltameter, we proceeded, in conjunction with Dr. McDaniel, to compare other forms with the porous cup form, especially the siphon and the Poggendorff, and to compare large and small voltameters of the same type. In nearly every case large voltameters gave larger deposits than small voltameters, and this phenomenon, which we called the volume effect, persisted even when the work was most carefully done with the purest silver nitrate available at that time. We noticed, however, that the volume effect was less with the purer salts, and we believed that with a solution strictly pure it would entirely disappear, as it should theoretically. Subsequent work has confirmed this belief, and we now regard the absence of the volume effect as one of the surest as well as one of the most rigorous tests of the purity of the electrolyte.

In the early part of our work we had used the purest silver nitrate which could be purchased, some from an American manufacturer and some from the Gold und Silber-Scheide-Anstalt, of Frankfurt, Germany. The latter salt gave a very beautiful crystalline deposit, and to chemical tests seemed to be of a high degree of purity and especially free from those impurities which we had found produced the most disturbing effects when added to the electrolyte. However, it gave a slight volume effect, and we believed it must contain some appreciable impurity. This led to an investigation of more delicate chemical tests for organic impurities in silver nitrate, which resulted in a new method which showed conclusively a small amount of reducing impurity in the silver nitrate, fully confirming the belief, based on the slight but undoubted volume effect, that the purest salt we had used was not quite pure enough for work of the highest precision.

This led to attempts to prepare still purer silver nitrate; that is, to get rid of the last traces of reducing impurity. Merely recrystallizing the salt repeatedly is not sufficient in all cases, unless certain special precautions are observed, but a method has been found (due in part to a suggestion from Mr. F. E. Smith) of obtaining silver nitrate so pure that it will show no volume effect and withstand the severe chemical test referred to above. This work is discussed in the third paper.

The work outlined above was carried out between October, 1908, and April 1, 1910. In the meantime an international investigation had been arranged to be carried out at the Bureau of Standards by representatives of four of the national standardizing laboratories, and we presented to the delegates selected, first in October, 1909, and again in April, 1910, on their assembling in Washington, a report of our work, and the conclusions we had reached on the subjects briefly indicated above. Work was carried on jointly during April and May of 1910 by the delegates, and the results obtained have been published in a separate report. We give in these papers mainly the results of our work up to the time the international delegates assembled in Washington, namely, April 1, 1910. We shall include results obtained since June 1, 1910, in the fourth paper of this series. On account of the salt employed in most of these earlier experiments not being quite pure we do not regard the numerical values obtained as final figures. They are, indeed, very nearly the same as we have found since, and as the international committee found, with very pure salt. But as this is an investigation of the silver voltameter as an instrument, and of the conditions necessary in order to secure normal results, we attach great weight to the numerical values given in the tables. The disturbances due to filter paper amount to from ten to a hundred parts in a hundred thousand. Avoiding filter paper and other organic septa and using an electrolyte so pure that there is no volume effect, the results are far more consistent, and the variations are reduced tenfold. There are still, however, some small uncertainties, due to slight impurities in the water employed, or to very slight acidity or alkalinity of the solution, or to gases absorbed by the electrolyte from the atmosphere, which we have investigated and upon which a report will be made in our final paper. This work will, we hope, indicate what the complete specifications for the official silver voltameter ought to be. April, 1910, will mark an important epoch in the history of the silver voltameter, namely, the close of the period of individual effort, extending from 1880 to 1910, in which many papers have been published and much learned concerning the theory and use of the silver voltameter. Beginning with 1910 we enter the period in which the national standardizing laboratories attempt by cooperation to perfect the silver voltameter as an electrical instrument of precision, and to agree upon specifications so complete and so precise that it may become in fact, as it is nominally, an international electrical standard.

III. QUANTITATIVE EXPERIMENTS, FIRST SERIES

A. APPARATUS

1. PLATINUM DISHES

We have used 10 platinum dishes and 2 gold dishes for cathodes or counterpoises. Four of these have a capacity of 350 cc and we have designated them as the "large bowls," 4 have a capacity of 175 cc and we call them the "medium bowls;" the 4 smallest, capacity 125 cc, are called the "small bowls" or crucibles. All of the dishes of any one size were adjusted to the same weight, so that they could be interchanged on the balance without requiring any transfer of weights. In the course of a long series of experiments, however, the medium-sized bowls lost several milligrams in weight which has been made up by certain small weights prepared for the purpose. The losses in weight of the other bowls have been much less. The time necessary to adjust the weight of the bowls was amply repaid by the convenience and speed with which accurate weighings could be made.

Two bowls, one large and one medium, were reserved in the balances for counterpoises, and deposits were never made in them. The small bowls were counterpoised by a sheet of platinum.

Table I shows the size and weight of the 12 dishes together with 4 others purchased since the experiments recorded in the present paper were completed.

TABLE I

Weights and Dimensions of the Platinum Dishes Used in the Experiments

No.	Designation	Approximate size			Material	Approximate weight
		Depth	Diameter	Capacity		
		cm	cm	cc		g
95	Large bowl	7	10	350	Platinum	80.27
94	.....do	7	10	350	.....do	80.27
93	.....do	7	10	350	.....do	80.27
92	.....do	7	10	350	.....do	80.27
25	Medium bowl	4	9	175	.....do	55.09
26	.....do	4	9	175	.....do	55.09
127	.....do	5	8	175	.....do	55.09
128	.....do	5	8	175	.....do	55.09
27	Crucible	7	6	125	.....do	39.11
28	.....do	7	6	125	.....do	39.11
125	.....do	7	6	125	Gold	39.11
126	.....do	7	6	125	.....do	39.11
36	Small bowl	6	6.4	140	Platinum	38.30
37	.....do	6	6.4	140	.....do	38.30
38	.....do	6	6.4	140	.....do	38.50
39	.....do	6	6.4	140	.....do	38.50

No. 94 and No. 25 were reserved for tare.

2. WEIGHTS

For weighing the deposits three weights designated as Ṡ, S̈, and Σ were used. The first two were of silver, gold plated, and were made to weigh about 4.098 grams, which is the approximate weight of silver deposited in one hour by a current numerically equal to the voltage of the Weston normal cell at 25°.0; that is a current, which, flowing through a 1-ohm standard, produces a difference of potential at the terminals equal to the electromotive force of the Weston cell. As the resistance of the 1-ohm standard varied slightly with the temperature at different times of the year and the Weston cells were kept at a slightly higher temperature in summer than in winter, the deposit was made as nearly as possible equal to the fixed weights by changes of a second or two in the length of the experiment. Later the current was reduced by one-half and the time of deposit made two hours, a 2-ohm standard being used. Σ was a collection of weights consisting of a 4-gram platinum piece, together with several weights from a fractional gram set known as "μ", the whole weighing about 4.095 grams. This was used exclusively for weighing deposits in the medium-size cups, as the 3 mg difference between this and Ṡ and S̈ was made up by the small weights added to the dishes, as mentioned above when they were weighed empty. A buoyancy correction was always made when using this weight.

These three weights have been compared with the standards of the bureau and found to have the following values:

TABLE II

Calibration of the Special Weights

Date	Ṡ	S̈	μ
	mg	mg	mg
Oct., 1908	....	....	4095.21
Jan., 1909	4098.26	4098.35	....
Apr., 1910	4098.26	4098.36	4095.23
Nov., 1911	4098.27	4098.37	4095.23

3. THE VOLTAMETERS

(*a*) **Rayleigh Voltameter.**—This form of voltameter consists of an anode of silver in a solution of silver nitrate contained in a platinum dish serving as cathode, any particle becoming detached from the anode being prevented from reaching the cathode by a sheet of filter paper. In some few cases we have used various textiles as linen, cotton, or silk in place of filter paper, and for convenience have classed them all under this head. Figure 1 shows this form of voltameter as we have used it.

We have used different kinds of filter paper, such as Eimer & Amend's "best white," C. Schleicher & Schull's No. 595, No. 602, No. 598, No. 590, and some papers especially prepared from given materials. In a few experiments we have also used filter tubes, such as are employed in the Soxhlet extraction apparatus.

Large bell jars cover the voltameters and stands during the progress of the experiment.

(*b*) **Richards Type.**—The Richards voltameter differs from the Rayleigh in employing a porous cup of unglazed porcelain as the means of separating the anode and cathode. We have used

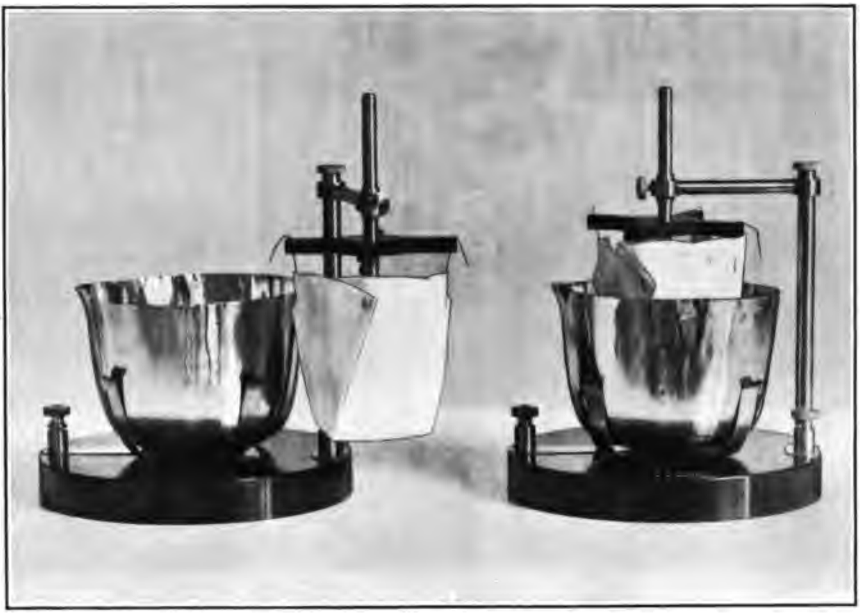

Fig. 1.—*The Rayleigh voltameter*

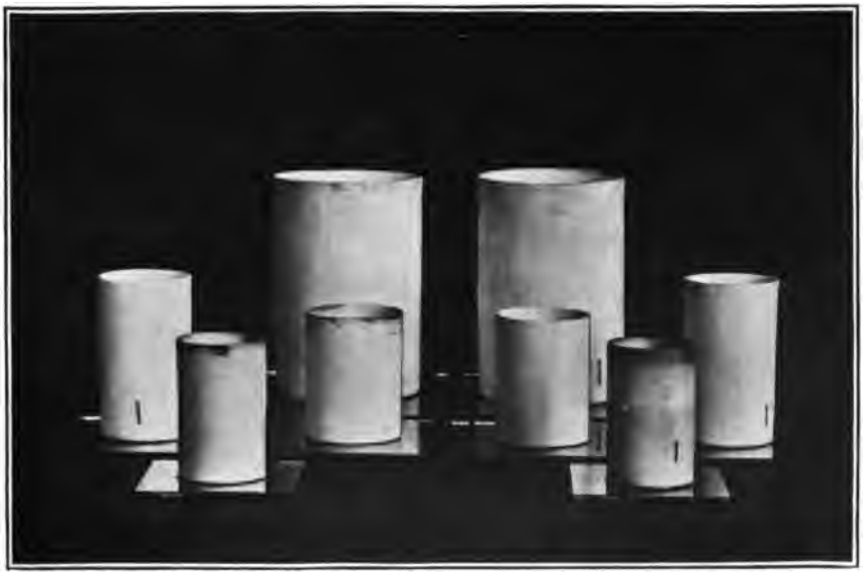

Fig. 2.—*The porous cups used in the Richards voltameter*

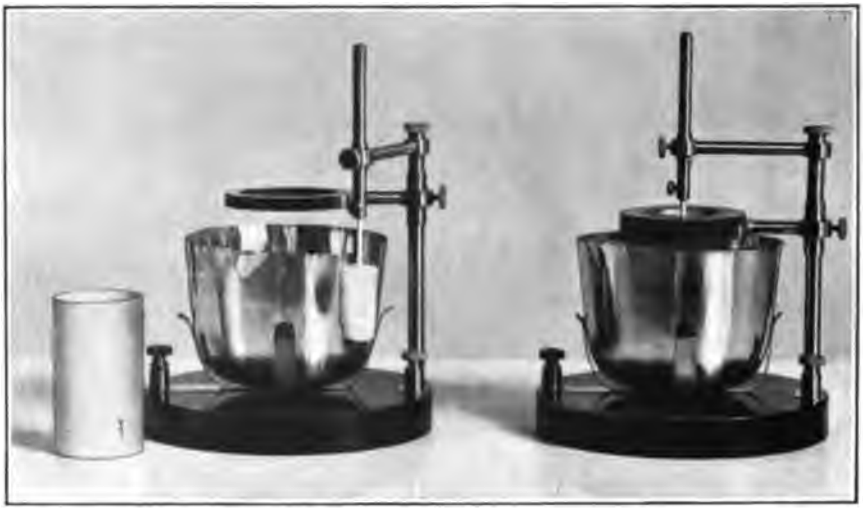

Fig. 3.—*The Richards voltameter, large size*

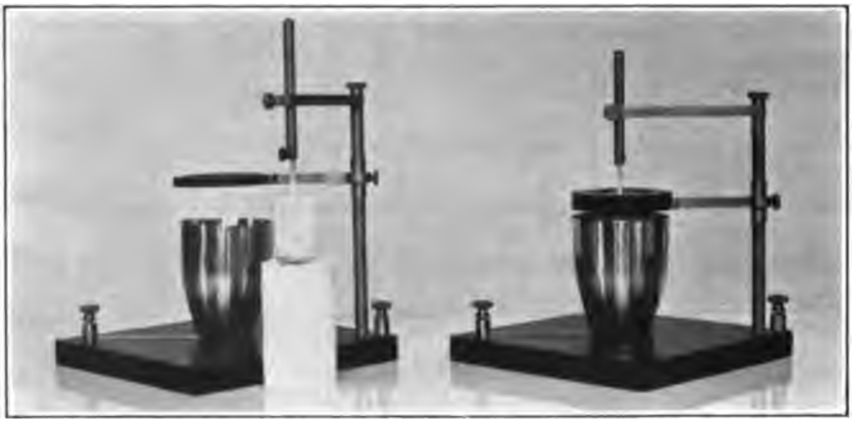

Fig. 4.—*The Richards voltameter, small size*

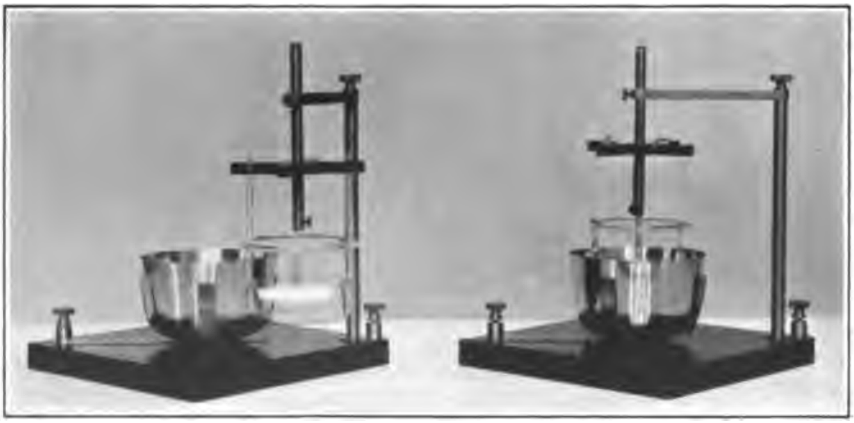

Fig. 5.—*The Poggendorff voltameter*

chiefly Pukal cups made by the Königlich Porzellan Manufaktur of Berlin. These are cylindrical, have thin walls, are of very fine grain, and of three sizes.

TABLE III

Dimensions of Porous Cups

Size	Diameter	Height
	cm	cm
Large	7	10.5
Medium	4	5
Small	3.5	5

The largest cups were used exclusively in the largest platinum bowls, but the smaller cups have been used in all the platinum dishes. They were white and without blemish before use.

The anode and cathode were mounted as in the Rayleigh form, but the porous cup was held in a split vulcanite ring made to fit closely around its top edge and supported from the same vertical rod as the anode. A large bell jar covers the voltameter when in use.

(*c*) **Poggendorff Type.**—The voltameter which we have designated as the Poggendorff type consists of silver anode and platinum bowl cathode, with electrolyte as above, but the only separation between the anode and cathode is a glass dish placed under the anode to catch any particles falling from it. We have in some few instances covered the top of the anode with a layer of silk, as we found that the glass dish was not always sufficient to confine the anode slime which is sometimes carried to the top of the electrolyte by bubbles of gas. Another way less open to objection of avoiding this difficulty was to support a ring of glass in the surface of the liquid. This prevented particles which came to the surface from floating out over the cathode space.

The mounting of the bowl and anode was the same as for the Rayleigh and Richards types, but the glass dish was supported by vertical rods of glass that hooked over ebonite arms projecting from the same support as the anode, so that at the end of the run all might be lifted out together. The ring of glass is sealed to the vertical glass rods at such a height as to be in the surface of the liquid when the voltameter is filled with electrolyte.

(*d*) **Siphon Type.**—The platinum dish serving as cathode and a ring of silver as anode are connected electrically by a column of electrolyte contained in a large glass siphon. The two sizes of siphons that we have used have been as follows:

Size	Axial length	Diameter	Capacity
	cm	cm	cc
Large	18	3.7	166
Small	10	2.2	44

These siphons were fitted with stopcocks to facilitate filling and emptying.

The siphon voltameter presents a serious difficulty in making absolute determinations by reason of the high resistance and consequent heating of the column of liquid, even in the larger siphons. This makes it very difficult to maintain the current at a fixed value. It may of course be used in comparison with other forms without keeping the current constant, but even then a very pure electrolyte must be used, since the large volume of liquid tends to give very high values if slight impurities are present. This will be discussed more fully in the third paper under the head of "volume effect."

In using the siphon voltameter we have mounted the platinum cup in one of the usual holders, while the anode (clamped in the usual way, but turned to one side) is placed in a glass dish mounted on a block of wood beside the cathode. The siphon is held in a wooden clamp stand. After all the parts were in place the platinum cup and glass dish were filled with electrolyte which was then drawn up into the siphon by means of the stopcock. For the large dishes and siphons about 500 to 600 cc of electrolyte were required.

As modifications of this form we have tried putting a porous cup over the anode or cathode ends of the siphon.

4. WEIGHING ROOM AND BALANCES

The weighings were made in a balance room built in the basement especially for the purpose. One-half of this room which has massive concrete walls was lined with hollow tile, an additional air

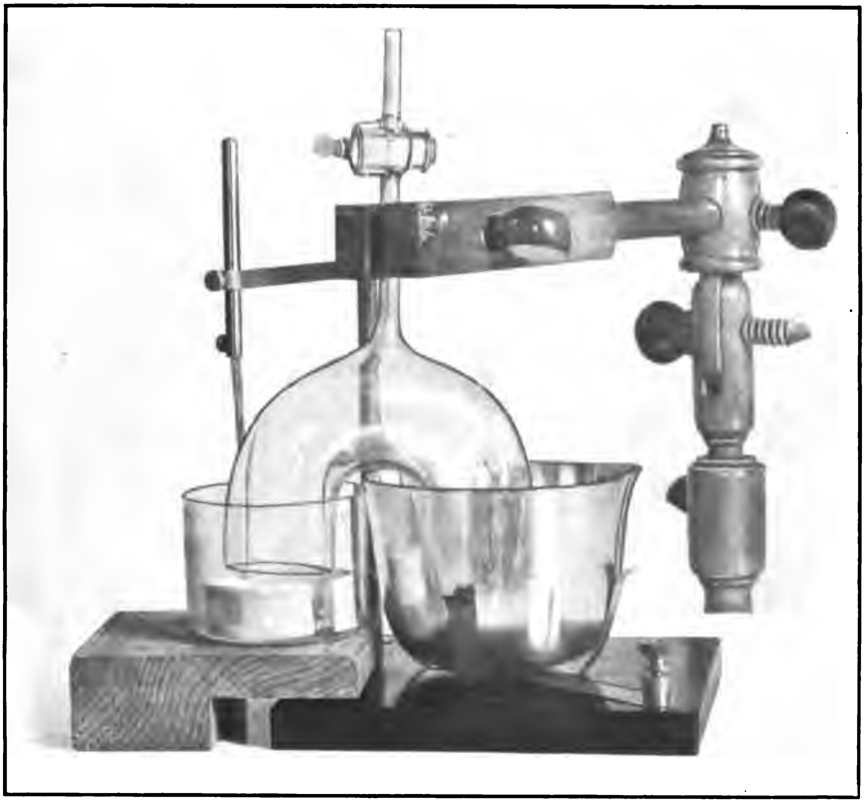

Fig. 6.—*The Siphon voltameter*

space being left between the tile and the concrete wall, and the tile plastered inside. A tile partition separates the balance room proper from the other end of the basement room, in the partition being double doors with vestibule between and two double windows.

Weighings were made from outside the balance room by observing the swings of the balances by means of telescopes extending through the windows. A plane mirror on the beam of the balance served to reflect a centimeter scale.

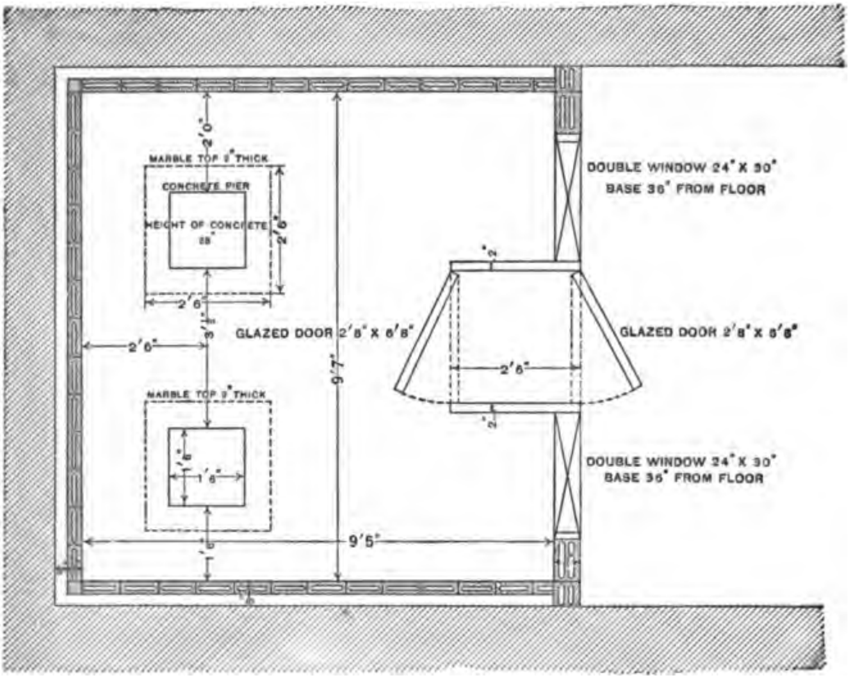

Fig. 7.—*Plan of the weighing room*

The temperature and humidity of the atmosphere inside the balance room were very constant, changing by only a few tenths of a degree and 1 or possibly 2 per cent, respectively, during 24 hours. They were recorded on a thermograph and hydrograph, of which sample records are shown.

If at any time the humidity became too high a drying apparatus holding about 50 pounds of calcium chloride was used to reduce it, but this was seldom required.

The balances were mounted on two marble-top piers independent of the foundations of the building. Three balances were used, each of 200 grams capacity. The first was by Oertling, the second by Rueprecht, and the third by Stückrath. Of these the Oertling has pans large enough to accommodate the largest platinum dishes used in the experiments and it was employed exclusively for weighing the four large bowls. All glass windows and doors on this balance are double to better protect the beam and platinum cups. The sensibility weight used on this balance was a 1-milligram rider always placed at division four and this four-tenths of a milligram produced a change in the equilibrium reading of 2.5 centimeters as read by telescope and scale.

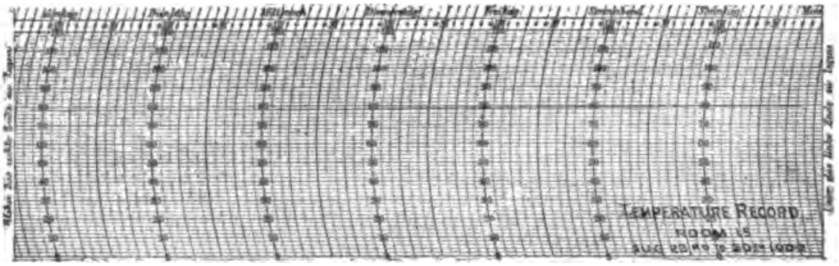

Fig. 8.—*Thermograph record of weighing room, August 23 to 30, 1909*

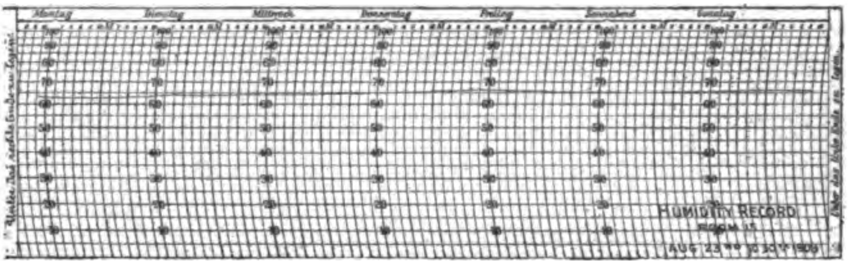

Fig. 9.—*Hydrograph record of weighing room, August 23 to 30, 1909*

The Rueprecht balance was best adapted to weigh the medium-sized bowls and was used for these alone. As the glass windows were single, the balance was further protected from radiations by heavy paper shields. A rider similar to that used on the Oertling was provided for this balance and its sensibility was about the same.

The Stückrath balance was used only for the crucibles, as its pans were small. It is arranged to be released and transpositions and changes of weights to be made from outside the room by means of rods and levers. All the glass windows and doors of the balance are double. The sensibility of the balance is about 16 scale divisions of 2 millimeters each for 1 milligram. Often all three balances were in use at the same time, one observer reading them and changing the loads in rotation. We described the method of making the weighings in the Report of the International Technical Committee, page 138.

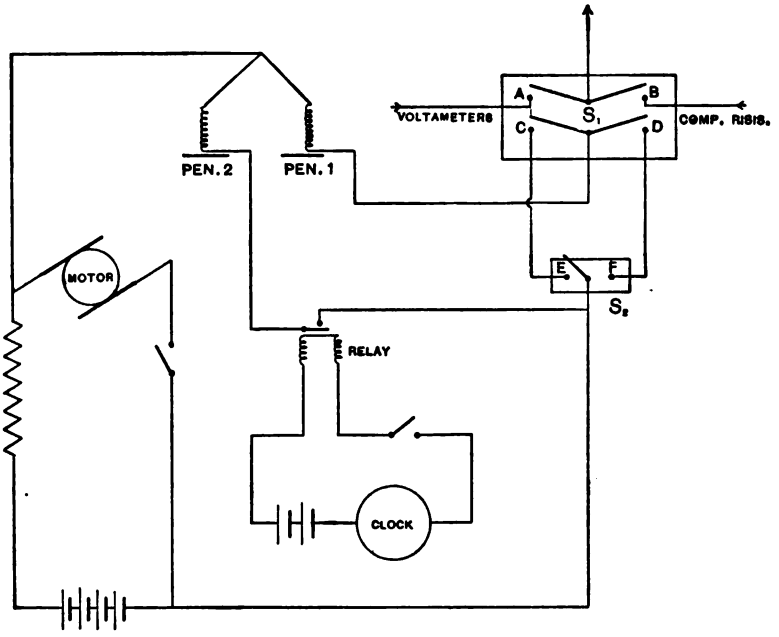

Fig. 10.—*Diagram of circuit for timing the duration of the experiments*

5. TIMING THE DEPOSITS

A quick, double-pole, double-throw switch serves to start the current through the voltameters and simultaneously to close another circuit which operates one of two pens on a chronograph. The two circuits were insulated from each other by the hard rubber yoke that united the blades of the switch. By reference to the diagram (Fig. 10) the operation of starting and stopping will be understood.

Before the beginning of the experiment the main switch S_1 is closed on the points B and D while the switch S_2 is on E. At the proper time the main switch is quickly thrown over to A and C. This starts the current through the voltameters and at the same time operates pen 1 of the chronograph. In order that the action of the chronograph pen may be the same at the start and at the end of the run the switch S_2 is then thrown from E to F. At the end of the experiment the main switch is thrown back to B and D. At the instant that the voltameter circuit is broken at A the pen circuit is made at D, and hence the first pen is again energized exactly as before. Thus any possible inequality in the working of the magnet on make and break circuit is avoided. The second pen records the ticks of the standard Riefler clock located in a constant temperature room in the basement. The rate of this clock as determined by frequent signals from the Naval Observatory was rarely over a tenth second per day, and was usually less. Hence no corrections to the time record are necessary. The chronograph used was made by the Société Génèvoise.

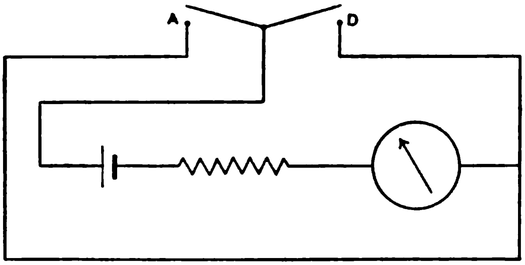

Fig. 11.—*Diagram of circuit for estimating the error of the timing device by ballistic method*

Since we regarded the insulation of the timing device from the main voltameter circuit as necessary to avoid possible stray currents, the accuracy with which the duration of an experiment is recorded depends on the mechanical perfection of the main switch S_1. The possible errors introduced by the switch can be tested experimentally by the following method shown diagrammatically (Fig. 11).

The making of the current at D gives the time record for the breaking of the voltameter circuit at A, hence we must determine the interval between the breaking of the circuit at A and the making at D. A very small part of the divided voltage of a dry cell was applied to a ballistic galvanometer with megohm box in series, the circuit being completed through A. This of course produced a steady deflection of the ballistic galvanometer which was also the case when the switch was closed on D. By operating the switch as is ordinarily done at the beginning and end of an experiment any throw of the ballistic galvanometer would measure the quantity of electricity that would have passed through the galvanometer if the current had not been interrupted. No throw of the galvanometer was observed except when the switch was operated more slowly than was done in practice in the voltameter circuit. The sensibility of the arrangement was such as to reveal an interval of time of 0.004 of a second. This shows that the error in time due to the switch could not be greater than this, which is less than a millionth part of the usual time of a deposit, namely, two hours. For determining the interval between the closing of A and C the same method with some necessary modifications was used. Here also the time interval was inappreciable.

6. THE VOLTAMETER CIRCUIT

The voltameter circuit consisted of a large ballast resistance, the voltameters with a parallel circuit of equal resistance for use before the run, two separate means of measuring the current, either of which could be used singly or both together, and suitable rheostats for quickly making large changes in the current or small changes, as occasion might require. Some modifications were made in the arrangement of the circuit during the progress of the work, but in the most essential features it remained the same throughout. Figure 12 shows the diagram of the circuit as it was used during the latter part of the work when currents of one-half ampere were used.

The standard resistance has usually been a Wolff open coil No. 2626 of 1 ohm for a current of 1 ampere or No. 2342 of 2 ohms for a current of one-half ampere. These were immersed in an oil bath, kept stirred by a small motor. They were frequently compared with the reference standards of this Bureau. The temperature of the oil bath was read several times during an experiment and from the computed average temperature the value of the resistance was obtained from the known coefficient of the coils.

The standard cells, four in number, were kept in an oil bath at the uniform temperature of 25° in winter and 28° in summer by a thermostat regulating to 0°.01 C. They were frequently compared with the reference cells of this Bureau and showed a variation of only about 2 microvolts.

One pair of potential leads from the standard resistance passed to a Wolff potentiometer as described on page 128 of the Report of the International Technical Committee. The second means of measuring the current provided a higher sensibility (20 mm. for 1 part in 100 000) and avoided any errors introduced by the potentiometer such as may arise from the adjustment of the coils, thermoelectric forces, changes in battery current, etc. The standard cell was joined in series with a sensitive Siemens and Halske galvanometer, so that by depressing a key the voltage of the cell could be directly opposed to the drop in potential across the standard resistance. The telescopes of both galvanometers were near the apparatus for regulating the current, so that it could be held at the proper value by an observer at either telescope. On some occasions both were used together, the observer at the potentiometer holding the current and a second observer reading and recording the deflections of the direct balance. The mean deviation of the current from a constant value is only a few parts in a million, and the algebraic average of the deviations is not over one part in a million. Hence no correction is necessary to the value of the current computed from the mean value of the resistance standard and of the Weston Cell during the period of the experiment. The direct balance method is the more reliable, but no significant difference was ever found between them.

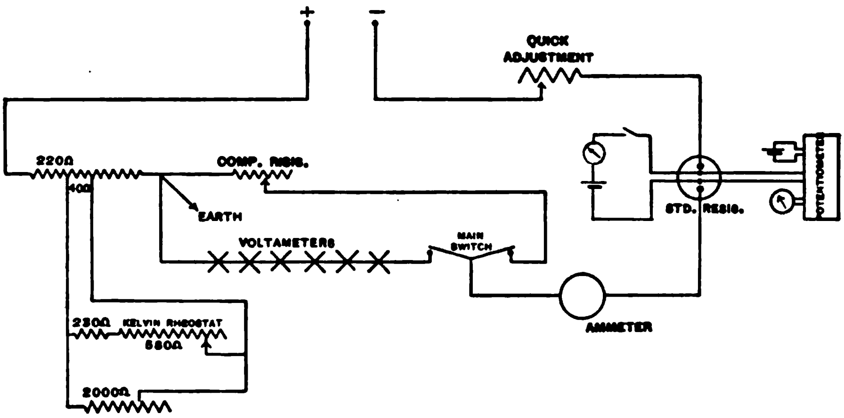

Fig. 12.—*Diagram of the voltameter circuit*

Insulation tests were made of all parts of the circuit at frequent intervals. The wiring was done especially with reference to high insulation. All wires passing from table to table or from one room to another were air insulated and supported only by vulcanite blocks fastened to wooden masts. All apparatus belonging to the circuit was mounted on vulcanite blocks. Further details as to the operation of the circuit are given in the Report of the International Technical Committee, page 126.

B. METHODS

1. METHOD OF WEIGHING

After drying the cups were allowed to come to equilibrium with the temperature and humidity of the balance case and room during several hours, because we believed that in the case of humidity it was better to weigh the cups in an undesiccated balance kept in a room of nearly constant humidity than to try to obtain weighings when the humidity in the balance case was changing every time it was opened, and the cup acquiring moisture during the process of weighing. Since, in every case, except for the smallest cups, the counterpoises were platinum dishes identical with those in use, and which always remained in the balance case, we believe the moisture deposited on counterpoise and cup to be the same when sufficient time for equilibrium to be established is allowed, and hence the humidity effect is eliminated. For the crucibles the counterpoise was sheet platinum, and hence this also approximated the best conditions.

The large surface of the cup makes it more difficult to weigh than the same mass of platinum in the form of a solid weight. Convection currents of air sufficient to introduce large errors in the result are set up by very slight differences in temperature. These may be caused either by the presence of the observer's body in making the necessary changes in the loads on the pans, or by light radiations falling on the surface of the cup. For this reason it was necessary to make the weighings in the constant temperature room which we have described. Even here it was necessary to allow the balance to swing from 10 to 20 minutes before reliable readings could be taken, as a drift of the equilibrium position was always apparent immediately after making changes in the loads on the pans.

The method of weighing adopted always involved an intercomparison of the weights of the several dishes, as well as a determination of their weights in terms of the counterpoise. The differences thus arising from experimental error were adjusted by least squares. If we designate three dishes, one of which (No. 94) is reserved for a counterpoise, by their numbers, No. 93, No. 95, and No. 94, we obtain the following equations:

$$\text{No. } 93 - \text{No. } 94 = a_1$$
$$\text{No. } 95 - \text{No. } 94 = a_2$$
$$\text{No. } 93 - \text{No. } 95 = a_3$$

If w_1 and w_2 represent the adjusted weight of No. 93 and No. 95 in terms of No. 94, we obtain the following equations for least square adjustment:

$$w_1 = \frac{1}{3}(2a_1 + a_2 + a_3)$$

$$w_2 = \frac{1}{3}(a_1 + 2a_2 - a_3)$$

Similarly for four dishes.[61]

The methods of making the observations are tabulated in the Report of the International Technical Committee, page 140.

2. METHOD OF RECORDING EXPERIMENTS

The form in which the records are preserved is as follows:

TABLE IV

Run of March 23, 1909

Holder	Cup	Anode	Septum	Electrolyte	Volume
					cc
A	92	Cup-shaped	Triple 598 f. p	Baker's 15%	335
B	93	do	Triple 595 f. p	do	335
C	95	do	Single 598 f. p	do	335
D	26	Disk	Single 595 f. p	do	175
E	28	Rod	Porous pot	do	95
F	27	do	do	do	95

Standard Cell No. 56 at 25°.04.

Standard Resistance No. 2342 at 21°.1 at start.

Standard Resistance No. 2342 at 22°.4 at end.

Time, 7199.74 seconds.

Current, 0.509426 ampere.

Room temperature, 20°.0.

Humidity, 34 per cent.

Appearance of deposit: No. 95, striated as usual, fuzzy like No. 26; No. 93, medium texture, very striated; No. 92, very striated; No. 26, fine texture, striations not marked, fuzzy; No. 27, very fine grain, no striations; No. 28, very fine grain, no striations.

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[61] U. S. Coast and Geodetic Survey Report for 1892, Appendix 10.

The current, time, and mass of deposit being known, we obtain at once the electrochemical equivalent from the formula.

$$\text{Electrochemical equivalent} = \frac{\text{Mass of deposit}}{\text{Current} \times \text{time}}$$

or the value for the Weston normal cell $\text{emf} = \dfrac{\text{Mass} \times \text{resistance}}{1.11800 \times \text{time}}$

TABLE V

Platinum bowl	Electrochemical equivalent
No. 95	1.11762
No. 93	1.11786
No. 92	1.11807
No. 26	1.11744
No. 27	1.11708
No. 28	1.11708

Nos. 27 and 28 are standard cups.

These values for the electrochemical equivalent have been computed from the value of the standard cell in use in the United States prior to January 1, 1911; that is, the voltage at 25° C equals 1.01890. On the basis used since that time we obtain for the value of the standard cell, assuming the electrochemical equivalent 1.11800 mg per coulomb and adding in a correction [62] of 3 in 10^5 as determined by the International Committee,

No. 27......1.01832 volts at 20°.

The deposits in the first four voltameters are obviously abnormal, due to the presence of filter paper, particularly in the case of No. 93 and No. 92, which had three times the quantity contained in No. 95 and No. 26. It is worthy of notice that filter paper No. 598, which gave larger values than No. 595, is a much heavier paper; that is, there is a greater mass of cellulose for the same size sheet of paper.

3. PREPARATION OF ANODES

The anodes were prepared for use in the quantitative experiments by depositing on them the silver from the bowls used in the preceding run. This provides an anode of great purity as well as affording a convenient and thorough method of cleaning the platinum dishes.

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[62] Report of International Technical Committee, p. 26.

In order that the electrolytic silver should adhere closely to the anode it is necessary, (1) that all traces of anode slime from previous use be removed; (2) that the anode be made bright and clean by a scratch brush; and (3) that only a small current be employed in depositing silver upon the anode. It is convenient to start this process in the evening and allow it to continue until the following morning.

After receiving the deposit of electrolytic silver the anodes are rinsed in a few changes of distilled water to free them from silver nitrate and then baked in an electric furnace to free them from acid and to reduce any traces of silver salts that may remain on them. It is convenient to heat them to redness for a few moments for this purpose, although a much lower temperature would be sufficient to eliminate the acid.

Upon anodes prepared in this way very little anode slime is produced. This is not a matter of great importance in the porous cup voltameter, but is more important in any form of voltameter in which no septum is used between anode and cathode.

4. METHOD OF PREPARING CATHODES

The platinum dish, after being electrolyzed as is described under the method of preparing anodes, is emptied of solution and as much as possible of the black crystalline growth that forms upon it after the silver has disappeared is washed out. The cups are then filled with strong nitric acid (equal parts of concentrated HNO_3 and water) and allowed to stand for about half an hour. Following this they are thoroughly gone over inside and out with a new piece of cotton cloth, rubber gloves protecting the cups from the hands. They are then quickly immersed in a 10 per cent solution of NaOH to remove any possible traces of grease, and afterwards rinsed in dilute HNO_3 to remove the last traces of the alkali. After thorough rinsing with tap water they are immersed in three changes of distilled water, of which the last two are double distilled and then placed in the oven to dry for three-quarters of an hour. During the latter part of this process they are handled entirely with tongs.

5. METHOD OF WASHING THE DEPOSITS

After the removal of the anode and septum from the voltameter the electrolyte is drawn off by a siphon into a small beaker bearing a letter to identify it with the particular voltameter. A few cc of electrolyte necessarily remain in the voltameter if floating silver is present, as this would otherwise be drawn over in the siphon. The dish is then filled with double distilled water. After all the voltameters have been thus dismantled the beakers containing the electrolyte are set on a sheet of black paper in a strong light and examined for loose silver particles. If any are found they are caught in a small pipette and put back into the platinum dish. The distilled water in the platinum bowls is then drawn off into large lettered beakers and then two or three more wash waters, according to the amount of electrolyte originally left in the voltameter, are used. The wash waters which have been collected are then examined for any particles of loose silver, as in the case of the electrolyte. After any such particles have been recovered and put back in the platinum bowl the process is repeated. Thus each voltameter is filled six or eight times with distilled water, of which the first and last two are double distilled. The last two or three never show any trace of $AgNO_3$ when tested with NaCl. After the last set of wash waters are examined the cups are removed to an electric oven for drying at 150°.

6. METHOD OF PREPARING THE POROUS POTS

The porous pots may be so thoroughly cleansed that they can stand for hours in distilled water without greatly increasing its conductivity. New porous pots of the best grade of unglazed porcelain will in general render the distilled water that they stand in alkaline. This is difficult to overcome by prolonged soaking in the best distilled water, but the process can be greatly shortened by letting dilute nitric acid filter through by gravity. This small amount of acid is easily washed out and a new pot, after such treatment for several days, is without effect on the conductivity of distilled water. As the porous pots are used from time to time they gradually become stained, particularly near the top. This, however, does not seem to affect the deposit of silver, as no certain difference has been detected between pots in constant use and others which were new and suitably treated. It is well, however, to clean and whiten them occasionally, and this may be safely done in two different ways, which require about the same time and are equally effective. By one method the porous pot is filled with equal parts of pure nitric acid and water, which is allowed to filter through slowly by gravity. If the pot is not entirely whitened the process should be repeated. The pot is then to be soaked in distilled water, changed several times a day until the water that has slowly filtered through it is neutral to iodeosine.[63] Then after allowing several portions of the best silver nitrate to filter through, it is ready for use in the voltameter. (The above method was developed during the course of the work, but was not used at first.)

By the other method the pot is freed from the silver nitrate contained in its pores by soaking it for several days in repeated changes of distilled water. When the water that has slowly filtered through it shows no reaction with sodium chloride or hydrochloric acid the pot is to be placed in a clean electric furnace and heated to bright red for about half an hour and then allowed to cool slowly in the furnace to avoid cracking. It should now be white. The alkalinity of the pot produced by baking is removed by soaking it in dilute nitric acid for about a day. When all traces of this acid have been removed, as is easily done with several changes of distilled water, the pot is prepared for use in the voltameters by filtering several portions of best electrolyte through its pores.

Pots cleaned by these two methods and compared with those long in use revealed no difference in the weight of silver deposited by a given quantity of electricity. The method of using Aqua Regia, KCN, HNO_3, and boiling water as recommended by Guthe[64] and subsequently used by Smith[65] with the addition of baking the pots to eliminate the acid, was unsatisfactory and abandoned. It requires a much longer time, owing to the soaking necessary to remove the acids and especially the KCN. After use in the voltameter the pots treated in this way are often stained yellow.

A convenient method of keeping the porous pots in good condition between experiments is nearly to submerge those of the same size in pure $AgNO_3$ in a crystallizing dish covered with a clock glass. After the run the porous pots are rinsed free from all traces of anode slime by a strong jet of distilled water. They are then rinsed with double distilled water and put to soak in the electrolyte again.

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[63] This test will be given in the third paper of this series by Rosa, Vinal, and McDaniel.

[64] This Bulletin, 1, p. 23.

[65] Collected Researches of N. P. L., 4, p. 141.

C. MANIPULATION TESTS

1. ERRORS OF STARTING, STOPPING, AND TIMING THE DEPOSITS

The quantitative work which began in October, 1908, was preceded by certain manipulation tests designed to show what accuracy could be obtained in the measurement of current and time, and in washing, drying, and weighing the platinum dishes.

To magnify the errors incident to starting, stopping, and timing the deposits, nine short runs aggregating about 10 minutes in length were made and weighed as a whole. The mean value of the three voltameters gave 1.11818 for the electrochemical equivalent. This was 69 parts in 100 000 higher than the values found from the two subsequent experiments of 1 ampere for one hour. Since the time is one-sixth and the number of runs 9 the proportional error for a one-hour run would be $\frac{69}{54}=1.3$ in 100 000. This error has probably been considerably reduced as the work has progressed.

2. COMPARISONS OF VACUUM DESICCATORS AND OVENS

Comparisons were made of drying the platinum dishes in vacuum desiccators over sulphuric acid and in an electric oven at 150° with results showing the superiority of the oven aside from the question of time saved. Three large platinum bowls prepared as if for a quantitative determination were allowed to dry in separate vacuum desiccators over night and then weighed against the usual counterpoise. They were then baked at 150° for 2¼ hours and weighed again with the following results:

TABLE VI

	No. 95—No. 94	No. 93—No. 94	No. 92—No. 94
	mg	mg	mg
Desiccator drying	−0.213	−0.134	0.000
After baking	− .316	− .214	− .089
Loss in weight	.103	.080	.089
After rebaking	− .321	− .218	− .093
Loss in weight	.005	.004	.004

Since 0.082 mg corresponds to 2 parts in 100 000 of the total deposit in a normal run the loss in weight found after the first

baking is too serious to neglect. The second baking, however, caused very little change.

Similar comparisons between vacuum desiccators and oven drying were tried with the bowls containing the deposit of a preliminary experiment. This showed better agreement between the two methods of drying. Immediately after finishing the washing of the deposit the cups were placed in separate vacuum desiccators and left over night. The following morning they were weighed and then baked at 150° for two hours and reweighed. The deposits were distinctly whiter after the baking. The results are as follows:

TABLE VII

Cup	After desiccation	After baking	Loss in weight
	mg	mg	mg
No. 95	4023.02	4022.99	0.03
No. 93	4023.23	4023.17	.06
No. 92	4022.86	4022.83	.03

Two reasons, however, led us to abandon the vacuum desiccator in favor of the oven. First, the oven was a much more expeditious method under our circumstances; second, we preferred to leave as much as 10 cc of double distilled water in the cups after washing the deposit, when, as often happened, there was loose silver floating on the surface of the water, rather than to drain the bowl and return the loose silver to the bowl.

3. WEIGHINGS

Throughout the course of the work the weighing of the cups was checked by observing the differences in weight of dishes that had been weighed singly against the counterpoise. Occasionally a whole new set of weighings was made and we present the following as typical. The first set is not as good as the average, but the second is perhaps a little better. The two sets are in satisfactory agreement since the maximum difference is equal to only 2.5 parts in a million of the deposit of silver.

TABLE VIII

Comparison Showing the Accuracy of Weighings

Nos. 127 and 128 were weighed against No. 25 on August 15, 1910.

mg
(1) No. 127—No. 25 = −0.092
(2) No. 128—No. 25 = − .319
(3) No. 127—No. 128 = + .207

From the first and second weighings,

Nos. 127—128 = +0.227

The least square adjusted values are—

No. 127—No. 25 = −0.099
No. 128—No. 25 = − .312

These cups remained in the balance until August 19, when they were reweighed.

mg
(1) No. 127—No. 25 = −0.092
(2) No. 128—No. 25 = − .312
(3) No. 127—No. 128 = + .228

From weighings (1) and (2)—

No. 127—No. 128 = +0.220

The least square of adjusted values are—

No. 127—No. 25 = −0.089
No. 128—No. 25 = − .315

Assuming that the tare No. 25 has remained constant during this time, we find the weights of the individual cups to be—

Date	No. 127	No. 128
	g	g
Aug. 15	55.089901	55.089588
Aug. 19	55.089911	55.089585

D. QUANTITATIVE RESULTS

1. LIST OF DEPOSITS

Between October 8, 1908, and September 22, 1909, we have made 27 separate runs with various forms of voltameters, having from 3 to 10 cups in use in each case. There were made in all 122 deposits, one of which was spoiled by the breaking of an especially tender filter paper. All the other deposits made or attempted (excluding a large number of qualitative deposits not intended to be weighed) have been tabulated.

The first 21 deposits made were in Rayleigh voltameters, using large platinum cups (weight 80 g, volume 350 cc) with the same silver nitrate and filter paper used in 1907. The mean value found for the electrochemical equivalent from these 21 deposits was 1.11749, almost identical with the mean found in 1907. The average variation from the mean was 5 parts in 100 000, showing a good degree of reproducibility when the same procedure is followed.

The next 100 deposits were made between December 22, 1908, and September 22, 1909, in which we studied the effect of filter paper in varying quantities in the voltameter and compared the Rayleigh and Richards forms, also varying the electrolyte, and changing numerous working conditions.

Table IX consists of a complete tabulation of the deposits made during this period. The values for the electrochemical equivalent of silver are our original results based on the value of 1.01890 volts for the Weston normal cell at 25° C, as was the practice in the United States prior to January 1, 1911. The means of the various tables following are converted into values for the voltage of the Weston cell computed upon the assumption of the electrochemical equivalent of silver being 1.11800 mg per coulomb, in accordance with the decision of the London Conference of 1908.

Table X contains a list of 43 deposits in the Rayleigh voltameter taken from the preceding general table. Thirty-seven of them were made using one sheet of filter paper, four using two sheets, and two using three sheets. The average value for the first set was 1.11745, of the second 1.11768, and of the third 1.11796. This shows that the excess of the deposit above the correct value is approximately proportional to the quantity of filter paper present.

Table XI gives a record of 53 deposits made in the porous cup form of voltameter, of which the first eight were contaminated with filter paper and three others were abnormal, Nos. 103, 109, and 117. The 42 normal deposits average 1.11704 for the electrochemical equivalent. This is a mean for large and small voltameters and different electrolytes. Most of it is 15 per cent new electrolyte, but a few deposits were made with used solutions. The large cups give a deposit which averages 2.5 in 100 000 greater than the small cups. This average is 40 parts in 100 000 lower than the value given by the filter paper voltameter.

TABLE IX

General Table of Quantitative Results for 1908 and 1909

Date	No.	Bowl	Form	Electrolyte	Time	Current	Deposit	El. Ch. Eq.	Remarks
1908					Seconds	Amperes	mg		
Oct. 8	1	95	Rayleigh	Baker 15%	3578.94	1.01931	4076.86	1.11755	Elmer & Amend's "Best white" filter paper used in first 22 deposits; all striated
	2	93	do	do			6.76	52	
	3	92	do	do			6.92	56	
12	4	95	do	do	3597.72	1.01931	4097.80	1.11742	
	5	93	do	do			7.92	46	
	6	92	do	do			7.82	43	
28	7	95	do	do	3602.88	1.01931	4103.72	1.11743	
	8	93	do	do			3.70	43	
	9	92	do	do			3.91	48	
Nov. 20	10	95	do	do	3601.69	1.01890	4101.25	1.11758	
	11	93	do	do			1.29	59	
	12	92	do	do			1.25	58	
Dec. 1	13	95	do	do	5712.01	1.01890	6503.66	1.11747	
	14	93	do	do			3.67	48	
	15	92	do	do			3.63	47	
8	16	95	do	do	7202.02	1.01893	8200.23	1.11745	
	17	93	do	do			0.01	42	
	18	92	do	do			0 39	47	
14	19	95	do	do	7200.28	1.01892	8198.66	1.11751	
	20	93	do	do			8.28	46	
	21	92	do	do			8.33	47	
22	22	95	do	do	3600.22	1.01886	4098.86	1.11743	
	23	93	Richards	do			8.29	27	
	24	92	do	do			8.11	23	
28	25	95	Rayleigh	do	3600.14	1.01891	4098.69	1.11735	S. & S. No. 595 filter paper
	26	93	do	do			8.55	31	S. & S. No. 602 filter paper
	27	92	do	do			8.55	31	E. & A. "Best white" filter paper

1909 Feb. 2	28	95	.....do	.....do	1 hour	1 amp.	4096.44	....	S. & S. No. 602 filter paper
	29	93	Richards	.....do			5.54	....	
	30	92	.....do	.....do			5.65	....	
	31	26	Poggendorff	.....do			9.96	....	Anode slime on cathode
	32	27	Richards	.....do			5.26	....	
	33	28	.....do	.....do			5.35	....	
11	34	95	Rayleigh	.....do	7210.28	.509432	4104.77	1.11751	S. & S. No. 602 filter paper
	35	93	.....do	.....do			5.54	72	S. & S. No. 602 filter paper, double
	36	92	Poggendorff	.....do			4.27	37	Striated
	37	26	.....do	.....do			4.05	31	Do.
	38	27	Richards	.....do			3.49	16	Slightly striated
	39	28	.....do	.....do			3.50	16	Do.
27	40	95	Rayleigh	.....do	7200.26	.509435	4098.60	1.11735	S. & S. 602 filter paper
	41	93	.....do	Kahlbaum 15%			8.86	44	Do.
	42	92	Poggendorff	Baker 15%			7.57	09	
	43	26	.....do	Kahlbaum 15%			7.14	698	
	44	27	Richards	Baker 15%			7.49	707	
	45	28	.....do	Kahlbaum 15%			7.84	17	
Mar. 11	46	95	Rayleigh	Baker 15%	7200.15	.509431	4099.89	1.11775	S. & S. No. 595 filter paper, double
	47	93	.....do	.....do			9.75	71	S. & S. No. 602 filter paper, double
	48	92	.....do	.....do			8.53	38	S. & S. No. 602 filter paper, single
	49	26	.....do	.....do			8.48	37	S. & S. No. 595 filter paper, single
	50	27	Richards	.....do			8.60	40	Probably contaminated
	51	28	.....do	.....do			8.61	40	Do.
23	52	95	Rayleigh	.....do	7199.74	.509426	4099.12	1.11762	S. & S. No. 598 filter paper, single
	53	93	.....do	.....do			4100.00	786	S. & S. No. 595 filter paper, triple
	54	92	.....do	.....do			0.77	807	S. & S. No. 598 filter paper, triple
	55	26	.....do	.....do			4098.49	744	S. & S. No. 595 filter paper, single
	56	27	Richards	.....do			7.17	708	Electrolyte not filtered through filter paper
	57	28	.....do	.....do			7.14	708	
Apr. 5	58	95	.....do	.....do	7199.99	.509428	4097.39	1.11710	Electrolyte free from filter paper contamination
	59	93	.....do	.....do			7.30	08	Do.
	60	27	.....do	.....do			7.29	07	Do.
	61	28	.....do	.....do			7.15	04	Do.

TABLE IX—Continued

General Table of Quantitative Results for 1908 and 1909—Continued

Date	No.	Bowl	Form	Electrolyte	Time	Current	Deposit	El. Ch. Eq.	Remarks
1909									
Apr. 9	62	95	Richards	Baker 15%	7200. 10	. 509430	4098. 61	1. 11741	Filter paper outside cup, striated
	63	93	do	do			7. 70	17	
	64	27	do	do			7. 62	15	
	65	28	do	do			7. 59	14	
16	66	95	do	do	7200. 07	. 509439	4097. 33	1. 11705	Filter paper inside porous cup
	67	93	do	do			7. 28	04	
	68	27	do	do			7. 26	03	
	69	28	do	do			7. 21	02	
24	70	95	do	Used solution	7200. 40	. 509436	4097. 56	1. 11707	No striations
	71	93	do	Baker 15%			7. 97	18	Do.
	72	27	do	do			7. 75	12	Do.
	73	28	do	Used solution			7. 54	06	Do.
May 6	74	95	do	do	7199. 98	. 509420	4096. 85	1. 11697	Electrolyte filtered through porous pot
	75	93	do	do			7. 01	702	Do.
	76	92	do	do			7. 56	16	Electrolyte not filtered, not clear
	77	26	do	do			8. 65	46	Electrolyte from Rayleigh voltameter
	78	27	do	do			7. 07	03	Electrolyte from Richards, not filtered
	79	28	do	do			6. 94	00	Electrolyte from Richards, filtered
18	80	95	do	Baker 15%	7199. 99	. 509392	4097. 07	1. 11709	Unused electrolyte
	81	93	do	Used electrolyte			6. 65	698	Electrolyte from Richards, filtered
	82	92	do	do			6. 59	697	Do.
	83	26	Rayleigh	Baker 15%			8. 49	748	5 sheets No. 590 filter paper, very thin
	84	27	Richards	Used electrolyte			7. 54	722	Filter paper outside porous cup
	85	28	do	do			7. 99	735	Electrolyte from Rayleigh voltameter
June 3	86	95	do	Baker 15%	7200. 24	. 509345	4100. 24	1. 11802	Filter paper soaked in electrolyte
	87	93	Leduc	do			0. 80	817	Linen bag around anode
	88	92	do	do			4098. 59	757	Silk bag around anode

	89	26	Rayleigh	do	7200.24	.509345	8.45	753	2 sheets No. 595 filtered paper
	90	27	Richards	do			6.44	698	Standard cup
	91	28	do	Used electrolyte			6.44	698	Not striated, fine grain
10	92	93	do	Baker 15%	7199.98	.509329	4096.57	1.11710	Standard cup, large
	93	27	do	Used electrolyte			6.27	702	Anode liquid from Richards
	94	28	do	Baker 15%			7.92	746	Silk soaked in electrolyte
Aug. 18	95	95	do	Frankfurt 15%	7199.97	.509361	4096.45	1.11700	Special distilled water
	96	93	do	Baker 15%			6.28	695	
	97	92	do	do			6.39	698	
	98	128	do	Frankfurt 15%			5.82	683	
	99	27	do	Baker 15%			6.23	694	
	100	28	do	Frankfurt 15%			6.11	689	
26	101	93	Rayleigh	do	7201.68	.509361	4098.38	1.11726	Linen paper, especially made
	102	92	do	do			7.96	14	Cotton paper, especially made
	103	128	Richards	do			7.99	15	Electrolyte contaminated
	104	27	do	do			7.39	699	Normal voltameter
	105	28	do	do			7.21	694	Do.
Sept. 9	106	95	do	do	7202.05	.509366	4098.32	1.11717	Normal voltameter, large
	107	93	Rayleigh	do			9.01	36	Little filter paper as possible
	108	92	do	do			9.72	55	Ordinary amount of filter paper
	109	128	Richards	do			8.57	24	Electrolyte contaminated
	110	27	do	do			8.21	14	Normal voltameter
	111	126	do	do			7.99	08	Do.
17	112	95	do	Baker 15%	7200.29	.509367	4096.89	1.11707	Do.
	113	93	do	do			7.23	17	Electrolyte filtered hot through filter paper
	114	92	Poggendorff	do			5.17	....	Lost silver
	115	26	do	do			7.87	....	Slime on cathode
	116	27	do	do			7.13	14	Very small anode
	117	28	Richards	do			6.82	05	Normal voltameter
22	118	127	do	Frankfurt 15%	2 hours	½ amp.	4100.26	....	
	119	128	Poggendorff	do			0.81	....	
	120	125	Richards	do			0.05	....	
	121	126	Poggendorff	do			0.61	....	

TABLE X

Rayleigh Voltameter

Date	No.	El. Ch. Eq.	Kind of filter paper
1908			
Oct. 8	1	1.11755	E. & A. "Best white"
	2	752	Do.
	3	756	Do.
12	4	742	Do.
	5	746	Do.
	6	743	Do.
28	7	743	Do.
	8	743	Do.
	9	748	Do.
Nov. 20	10	758	Do.
	11	759	Do.
	12	758	Do.
Dec. 1	13	747	Do.
	14	748	Do.
	15	747	Do.
8	16	745	Do.
	17	742	Do.
	18	747	Do.
14	19	751	Do.
	20	746	Do.
	21	747	Do.
22	22	743	Do.
28	25	735	S. & S. No. 595
	26	731	S. & S. No. 602, hard
	27	731	E. & A. "Best white"
Feb. 11	34	751	S. & S. No. 602, hard
	35	772	2 sheets No. 602, hard
27	40	735	S. & S. No. 602, hard
	41	744	Do.
Mar. 11	46	775	2 sheets No. 595
	47	771	2 sheets No. 602, hard
	48	738	1 sheet No. 602, hard
	49	737	1 sheet No. 595
23	52	762	1 sheet No. 598, very heavy paper
	53	786	3 sheets No. 595
	54	807	3 sheets No. 598
	55	744	1 sheet No. 595
May 18	83	748	5 sheets No. 590, very thin; equivalent to 2 sheets No. 595
June 3	89	753	2 sheets No. 595
Aug. 26	101	726	Unsized linen paper
	102	714	Unsized cotton paper
Sept. 9	107	736	Less than ordinary No. 595
	108	755	1 sheet No. 595

Mean of 43=1.11749.
Mean of 37=1.11745, with 1 sheet of filter paper.
Mean of 4=1.11768, with 2 sheets of filter paper.
Mean of 2=1.11796, with 3 sheets of filter paper.

Taking the value obtained for the normal Rayleigh voltameter (e. g., with 1 sheet of filter paper) we find the voltage of the Weston normal cell at 20°, assuming the electrochemical equivalent of silver to be 1.11800 mg per coulomb, is 1.01866 volts.

TABLE XI

Richards Voltameter

(The electrolyte for the first eight deposits was filtered through filter paper. For the others no filter paper was used, except as noted, and in most cases the electrolyte was not filtered. The large, medium, and small voltameters are denoted by l, m, s, respectively.)

Date	No.	Size	El. Ch. Eq.	Remarks
Dec. 22	23	l.	1. 11727	Porous cups soaked in used electrolyte from Rayleigh voltameter
	24	l.	722	
Feb. 11	38	s.	716	
	39	s.	716	
27	44	s.	707	
	45	s.	717	Kahlbaum $AgNO_3$
Mar. 11	50	s.	740	Electrolyte probably contaminated
	51	s.	740	Do.
23	56	s.	708	Discontinued use of filter paper for filtering electrolyte
	57	s.	708	
Apr. 5	58	l.	710	
	59	l.	708	
	60	s.	707	
	61	s.	704	
9	63	l.	717	
	64	s.	715	
	65	s.	714	
16	66	l.	705	(Filter paper inside of porous cup)
	67	l.	704	
	68	s.	708	
	69	s.	702	
24	70	l.	707	Used solution
	71	l.	718	New solution
	72	s.	712	Do.
	73	s.	706	Used solution
May 6	74	l.	697	Used electrolyte, filtered through porous cup
	75	l.	702	
	76	l.	716	Used electrolyte, not filtered, not clear
	78	s.	703	Used electrolyte, not filtered, clear
	79	s.	700	Used electrolyte, filtered
18	80	l.	709	New electrolyte
	81	l.	698	Used electrolyte filtered through porous cup
	82	l.	697	Used electrolyte, filtered
June 3	90	s.	698	New electrolyte
	91	s.	698	Used electrolyte
10	92	l.	710	New electrolyte
	93	s.	702	Used anode electrolyte

TABLE XI—Continued

Richards Voltameter—Continued

Date	No.	Size	El. Ch. Eq.	Remarks
Aug. 18	95	l.	1.11700	Frankfurt salt
	96	l.	695	Baker salt
	97	l.	698	Do.
	98	m.	683	Frankfurt salt
	99	s.	694	Baker salt
	100	s.	689	Frankfurt salt
26	103	m.	715	Electrolyte contaminated
	104	s.	699	Frankfurt salt
	105	s.	694	Do.
Sept. 9	106	l.	717	
	109	m.	724	Electrolyte contaminated
	110	s.	714	
	111	s.	708	
17	112	l.	707	
	113	l.	717	Electrolyte filtered hot through filter paper
	117	s.	705	
Mean of 42........			1.11704_3	

Average difference = 2½ in 100 000 between large and small in same runs.

The mean of these 42 determinations gives for the value of the Weston normal cell at 20° 1.01828_7 volts. The first eight and Nos. 76, 103, and 109 have been omitted in taking the mean.

TABLE XII

Summary of Miscellaneous Deposits

Date	No.	El. Ch. Eq.	Remarks
1909			
Apr. 9	62	1.11741	Baker salt, small voltameter with porous cup, having strip of filter paper 50 by 6½ cm wrapped around outside of latter
May 6	77	1.11746	Porous cup used electrolyte from Rayleigh voltameter
18	84	1.11722	Used electrolyte, with filter paper 30 by 5 cm wrapped around porous cup
	85	1.11735	Used electrolyte from No. 62
	86	1.11802	New Baker electrolyte, 2 sheets of filter paper soaked over night in electrolyte
	87	1.11817	Linen bag around anode, as used by Leduc
	88	1.11757	Silk bag around anode
June 10	94	1.11746	New Baker electrolyte 15 per cent raw silk soaked in it over night
Mean of 8.		1.11758	

Weston cell at 20° = 1.01878.

Table XII gives a list of eight deposits, in some of which filter paper was placed in the electrolyte outside the porous cup, or a filter paper solution was used in a porous cup form, or a silk or linen bag was used instead of filter paper or a porous cup. In every case the deposit is too heavy; in two cases by nearly one-tenth per cent.

Table XIII gives the results of 10 deposits in the Poggendorff form of voltameter, 3 of which were failures. The value of the equivalent as given by a porous cup voltameter is also given (in one comparative run the latter is assumed as 1.11703). The mean value is somewhat higher than the porous cup form has given.

TABLE XIII

Summary of Poggendorff Form, Without Silk Septum

Date	No.	El. Ch. Eq.		Remarks
		Poggendorff	Porous pot	
1909				
Feb. 2	31	....	....	Deposit 4 mg too heavy, anode slime on cathode
11	36	1. 11737	716	Deposit striated Baker salt 15 per cent
	37	731	716	Deposit striated
27	42	709	707	Baker salt 15 per cent
	43	698	717	Kahlbaum salt 15 per cent
Sept. 17	114	....	....	Deposit 1.7 mg too light, silver lost
	115	....	....	Deposit 1 mg too heavy, anode slime
	116	714	705	Good deposit
22	119	721	703	Do.
	121	716	703	Do.
Mean of 7.		1. 11718	709	

Weston cell at 20° = 1.01841 volts.

The electrolyte was not quite pure, so that the deposit should have been a little too heavy. The small porous cup voltameters in use at the same time for comparison gave 1.11709, or 8 parts in 100000 less.

2. NARRATIVE OF THE TRIALS OF FILTER PAPER, ETC.

Between October 8 and December 14, 1908, seven experiments were made using three large Rayleigh voltameters, all assembled under as nearly identical conditions as possible. The current and time were accurately measured and were 1 ampere and one hour, respectively, thus depositing about 4.098 grams of silver. The result of these experiments was to show a very fair degree of reproducibility, but the value obtained for the electrochemical equivalent of silver was considerably in excess of that found by Smith, Mather, and Lowry.[66] On December 22 two porous pots made by Königlich Porzellan Manufaktur of Berlin were used for the first time.

The values obtained with the porous pots were almost 2 in 10 000 smaller than with the filter paper. This suggested that the "Best white" filter paper which we had been using up to this time might not be sufficiently good. In the next run of December 28, 1908, we therefore compared it with No. 595 S. & S. and No. 602 S. & S. and found all in substantial agreement. A further comparison of filter paper and porous cups on February 2, 1909, confirmed the conclusions of the preceeding runs that the Rayleigh voltameter gives a higher deposit than the porous cup type. We supposed at this time that this was due to the filter paper not acting as a perfect separator of the anode and cathode solutions as has been suggested by Richards.[67] In the hope of rendering the filter paper more efficient in this regard we tried in succeeding experiments the effect of doubling or even trebling the thickness. But instead of agreeing better with the result obtained with the porous cup, the deposits were still heavier, two sheets of filter paper giving an excess of about double, and three an excess about treble that due to one sheet. That is, the excess in weight was proportional to the quantity of filter paper, and was therefore not due to the filter paper being an imperfect filtering medium. This result also followed when the finest grades of filter paper were used, the excess weight above the normal weight in a Richards voltameter being practically the same for all filter paper tried, if the weight of filter paper submerged in the electrolyte was the same. The excess weight of silver, with a relatively large amount of filter paper, may be as much as 0.1 per cent. Striations are more marked as the quantity of filter paper is greater, so that one can predict a heavy deposit by its appearance.

This evidence, which seemed to indicate that the filter paper voltameter was giving abnormally high values for the electro-

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[66] Collected Researches, N. P. L., **4**, p. 157.

[67] Proc. Am. Academy, **35**, p. 123. **37**, p. 415.

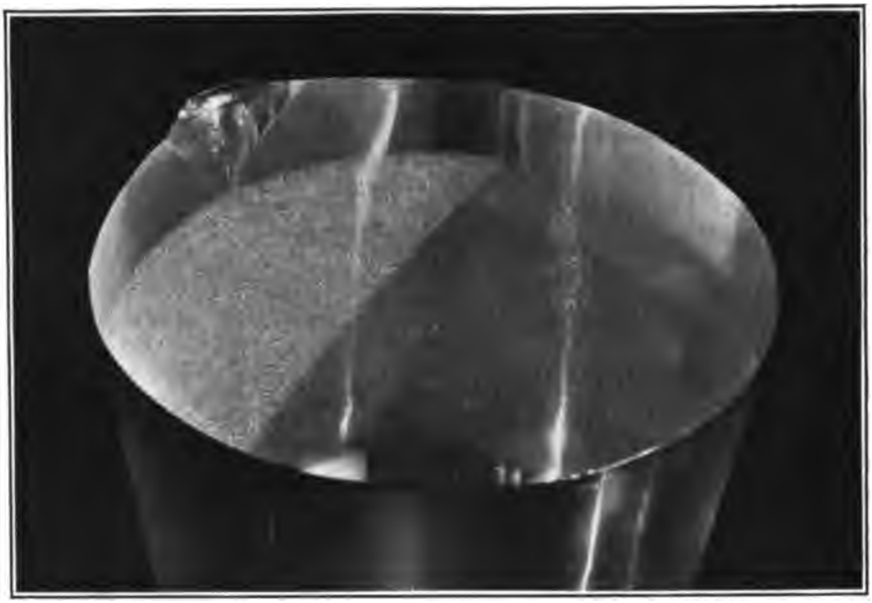

Fig. 13.—*Characteristic deposit in Richards voltameter. The electrolyte had been previously used in a voltameter free from filter-paper contamination*

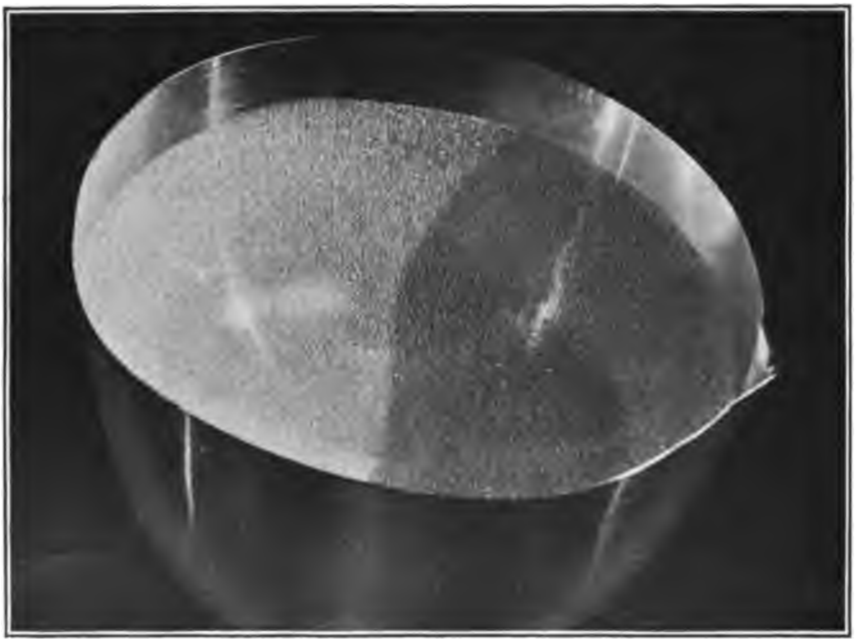

Fig. 14.—*Striated deposit made in a Richards voltameter from an electrolyte previously used with filter paper*

chemical equivalent, was confirmed on April 9 and 16, when we compared voltameters having both the porous cup and filter paper with the ordinary porous cup type. In the former experiment a strip 50 by 6.5 cm of No. 602 S. & S. filter paper was wrapped around the outside of the porous cup. The deposit in this voltameter was strongly striated and 26 parts in 100 000 heavier than the mean of the three normal Richards, which agreed closely among themselves and were free from striations. On April 16 a similar experiment was performed, differing only in the fact that the strip of filter paper was placed inside of one of the porous cups. The four deposits of this run were all fine grain and free from striation and the maximum difference in weight between any two is only 3 parts in 100 000. These results were confirmed by a subsequent experiment on May 18.

Having thus satisfied ourselves that filter paper is capable of exercising a profound effect on the appearance and weight of the deposit, we were naturally led to inquire whether it was necessary to have the paper present at the time the electrolysis was actually in progress. We obtained the first definite knowledge that such was not the case on May 6, when we electrolyzed for the second time the cathode solution that had been used in the combined porous cup-filter paper voltameter of April 9. This time the electrolysis was made in a normal Richards voltameter and was compared with solutions that had been used previously with porous cups only. The results of this experiment were very conclusive. The deposit from the electrolyte contaminated with filter paper was again strongly striated and gave a value for the electrochemical equivalent that was characteristic of the Rayleigh voltameter, while the others gave nonstriated deposits of what we believed to be about the normal weight. Two contrasted deposits of this run are shown in photographs, figures 13 and 14. The results of this experiment justified the conclusion which we had previously reached, that it was unwise to filter the electrolyte through filter paper before use. This practice had been discontinued beginning with the run of March 23, 1909, and since that time we had been obtaining lower values for the electrochemical equivalent with the Richards voltameter.

On June 3 and June 10 we began to try other substitutes for filter paper, particularly linen and silk textiles. In the former of these two runs we inclosed the anodes in silk and linen bags as was done by Leduc and compared them with a Richards voltameter taken as standard. We also electrolyzed at this time 340 cc of the same electrolyte in which two sheets of 19 cm No. 595 S. & S. filter paper had been allowed to soak over night. This was done in a Richards voltameter. The deposits from the silk and the linen were both abnormally high, the latter being more than 0.1 per cent higher than the standard voltameter, but this may have been due in part to some anode slime passing through the meshes of the cloth.

The deposit from the electrolyte contaminated with filter paper was also 0.1 per cent heavy. The sides of this cup were more heavily striated than any we had seen up to this time and the bottom was covered with stiff vertical rods of silver several millimeters long. (See Fig. 15.)

On June 10 we compared the deposits from an electrolyte in which some of the same sample of silk as used in the previous run had been soaked over night, with a normal voltameter, and also with a voltameter in which the electrolyte was anode solutions saved from previous runs and free from filter paper contamination. This last was tried because we believed that if a complex ion were really present in the anode liquid we should get an abnormally heavy deposit. This, however, we did not find, but in fact it gave a lower deposit than the standard cup. In appearance, weight, etc., it behaved like the used cathode liquid reelectrolyzed in some previous experiments. (See Fig. 16.) The result of the silk test was a deposit very abnormal in weight and appearance. (See Fig. 17.)

3. USED SOLUTIONS

Further evidence of the action of filter paper and similar substances in increasing the weight of the deposit was obtained by reelectrolyzing certain of our old solutions saved from previous experiments. Many observers[68] have recorded an increased deposit from solutions electrolyzed two or more times. This we believe to have been due to contamination of the solution with filter paper, because in our earliest work done during the summer

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[68] Novak, Proc. Roy. Bohemian Ac. Sci. Prague, 1, p. 387; 1892. Rodger and Watson, Phil. Trans. A, 186; 1895. Kahle, Zeitschr. f. Inst. 18, p. 229; 1898. van Dijk, Ann. d. Phys. 19, p. 249; 1906. Guthe, Phys. Rev. 19, p. 138; 1904. This Bulletin, I, p. 355; 1904.

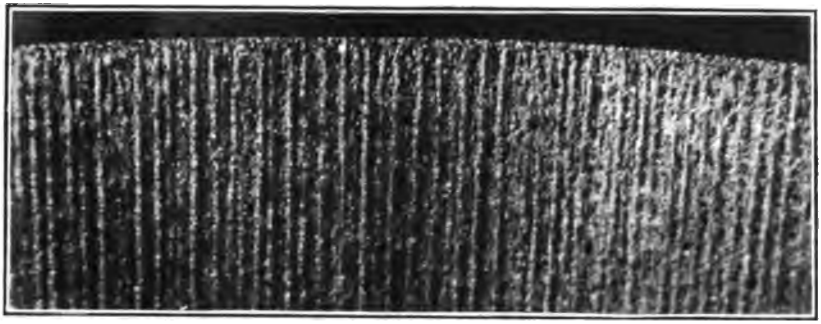

Fig. 15.—*Heavy striations due to excess of filter paper*

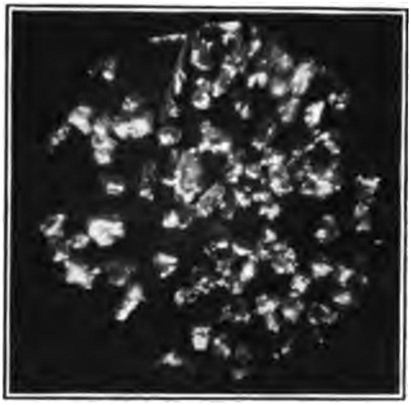

Fig. 16.—*Showing a normal crystalline deposit from an electrolysis of anode solution.* ×*16*

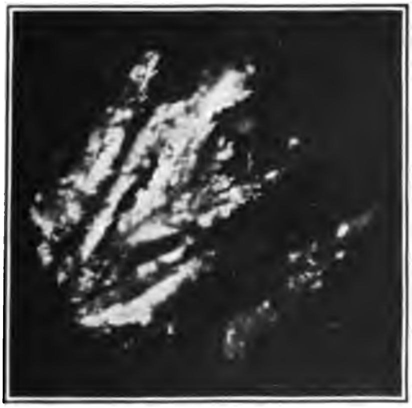

Fig. 17.—*Showing the effect of silk in changing the crystalline character of the deposit.* ×*16*

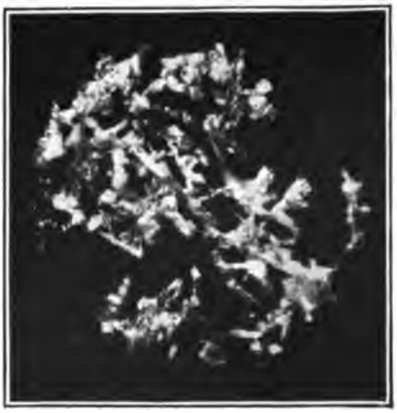

Fig. 18.—*Showing the modification of crystalline structure due to filtering the electrolyte hot through filter paper.* ×*16*

of 1907 we observed this increase many times while we were using the Rayleigh type of voltameter. We found for the means of new and used solutions

34 deposits unused solutions.....	1.11746
21 deposits used solutions.......	1.11761

But on the other hand we have repeatedly used solutions saved from the Richards voltameters of previous runs and have found the deposit to be substantially normal in weight and appearance, tending rather to be lighter in weight than heavier. Since in this latter case we were dealing with solutions that had not been in contact with filter paper we believed this to be an added proof that filter paper is an active agent in the voltameter. Smith [69] found that long continued electrolysis is without effect upon the deposits made subsequently with the same electrolyte, but it is to be noted that in performing this experiment he omitted the use of filter paper in the major part of the experiment.

During the quantitative work of 1909 we made eight determinations of the electrochemical equivalent with used solutions saved from the Richards voltameter and which were therefore free from filter paper contamination, and at the same time five determinations with new solutions with results as follows:

TABLE XIV

Date	Size	New electrolyte	Used electrolyte	Remarks
1909				
Apr. 24	l.	1.11718	....	Baker $AgNO_3$
	s.	712	....	Do.
	l.	....	1.11707	Cathode liquid
	s.	....	706	Do.
May 6	l.	....	716	Electrolyte not clear, omitted
	s.	....	703	Cathode liquid
18	l.	709	....	Baker $AgNO_3$
	l.	....	698	Cathode liquid
	l.	....	697	Do.
June 3	s.	698	....	Baker $AgNO_3$
	s.	....	698	Cathode liquid
10	l.	710	....	Baker $AgNO_3$
	s.	....	702	Anode liquid
	Mean	1.11709	1.11702	

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[69] Collected Researches, Nat. Phys. Lab. Vol. IV, p. 164.

In the column headed "size" the letters l and s are used to denote the large bowls and small bowls, respectively. The crystals from used electrolyte are well formed but usually finer; that is, there are more to the square centimeter of area than in the other case.

Repeated electrolysis makes the deposit still finer in grain. On November 3, 1909, we assembled a voltameter with 100 cc of pure unused electrolyte as if for a quantitative run. We made four runs at 1 ampere for one hour each with this electrolyte, examining and removing the deposit between each run. As the 100 cc of 15 per cent solution contained at the start 11.2 grams of silver and during the four experiments we removed 16 grams, this served as a test of complete exhaustion. The deposit from each successive run was finer than that of the preceding. At the end of the fourth experiment the electrolyte was neutral to methyl orange after precipitating the silver with neutral KCl solution and filtering. Apparently the acid plays an important rôle in diminishing the size of the crystals, as only very small amounts are required, but it also seems possible that this decrease in size of the silver crystals is due in part to the decrease in concentration of the electrolyte outside the porous pot. We have found that concentration, like current density, exercises a marked influence upon the size of the crystals. This may not, however, be the whole explanation of the phenomena, since the deposit seems to be slightly lighter in weight as well as of finer grain. We have made quantitative comparisons of deposits from different concentrations without being able to detect any certain difference in weight.

Aside from the small changes in weight and appearance continued electrolysis is an effective method for purifying a badly contaminated solution. In a series of experiments[70] on a solution contaminated with filter paper, electrolyzing the solution repeatedly, we were able to observe this purifying effect, as the deposit gradually changed from the strongly striated molten appearance at first to a somewhat crystalline and slightly striated stage, and finally to a state of complete freedom from striations and well-defined crystalline deposit. Using solutions that we knew to be slightly impure we have made them give values for the electrochemical equivalent more nearly consistent with what we believe the correct figure by this preliminary electrolyzing process. Two such samples of $AgNO_3$ were put in Richards voltameters and 8 grams of silver deposited. The cathode liquid was then drawn off and used in several voltameters in a quantitative experiment. Omitting one voltameter, which was obviously abnormal, we have:

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[70] Described in the second paper of this series by Rosa, Vinal, and McDaniel.

TABLE XV

Effect of Electrolysis on Impure Solutions

Original Baker	1.11711	**Original Frankfurt**	1.11706
Electrolyzed Baker	1.11708	**Do**	1.11706
Do	1.11708	**Electrolyzed Frankfurt**	1.11700

4. USE OF FILTER PAPER IN FILTERING

Smith[71] in his description of a standard method of preparing silver nitrate makes the following statement:

> For filtering the hot solution we prefer to use a Hirsh porcelain funnel, the perforated plate of which is covered by two disks of filter paper.

We believed that the electrolyte might be sufficiently contaminated in this way to render the results unreliable, and accordingly tried the following experiment: The electrolyte for one cup of the run of September 17, 1909, was mixed hot and concentrated and then filtered, as described by Smith. Afterwards it was cooled and diluted to 15 per cent and electrolyzed in a Richards voltameter. The excess weight of 1 in 10 000 over the normal Richards, as well as the appearance, shows that the deposit has been affected by the filter paper. To the unaided eye the deposit looks woolly and striated. A magnified sample of it is shown in figure 18.

The conclusions of our work with the Rayleigh voltameter have made it evident, we believe, that for work of high accuracy any voltameter containing filter paper or similar substance is to be avoided, and that in the preparation of silver nitrate care must be exercised to keep it free from contamination by filter paper.

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[71] Collected Researches, N. P. L., 4, p. 163.

IV. CONCLUSIONS

In this first paper we have briefly reviewed the work of preceding investigators and have described our own methods of work. We have recorded all of the quantitative measurements up to and including September 22, 1909. This first series of experiments definitely established the following facts:

1. That the filter paper voltameter as ordinarily used, gives a relatively large excess of deposit over the porous pot form.
2. That this excess is due directly to the chemical activity of the filter paper and not to its failure to confine the anode products.
3. That in using two or three thicknesses of the paper the effect is approximately doubled or trebled.
4. That the deposits from relatively pure solutions are crystalline and not striated, while deposits from solutions contaminated with filter paper, linen, or silk are noncrystalline and striated.
5. That it is not necessary that the filter paper should be present in the voltameter at the time of electrolysis to produce its effects, if the solution has been previously in contact with it.
6. That repeated use of the same solution in the filter paper voltameter yields an increasing excess of deposit owing to the increasing contamination of the electrolyte.
7. That a contaminated solution may on the other hand be rendered less impure by electrolysis in the absence of organic material.
8. That anode solutions saved from the porous cup voltameters may be used as the electrolyte in a voltameter without yielding any excess of weight or making the deposit striated.
9. That the appearance of the deposit is a valuable criterion of the purity of the electrolyte.

The next paper of this series will deal at length with the chemical questions involved in the filter paper voltameter and a theory will be given as to why a contaminated electrolyte yields a deposit differing in appearance from the normal crystalline one. Following this will be given the second series of experiments leading up to the work of the International Technical Committee, April 1, 1910. This work was chiefly a comparison of different types of voltameters and a study of the purity of the electrolyte for which some rigid criteria will be given. Finally the observations made since the committee adjourned will be given. In this the effect of acid and alkali in the electrolyte have been studied and a number of deposits made using the approved types of voltameter with electrolytes of the highest purity for the determination of the electromotive force of the Weston normal cell and the absolute electrochemical equivalent of silver.

WASHINGTON, August 1, 1912.

THE SILVER VOLTAMETER—PART II

THE CHEMISTRY OF THE FILTER PAPER VOLTAMETER AND THE EXPLANATION OF STRIATIONS

By E. B. Rosa, G. W. Vinal, and A. S. McDaniel

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I. THE QUALITATIVE EXPERIMENTS WITH THE SILVER VOLTAMETER

A. INTRODUCTION

The qualitative work with the voltameter began early in July of 1909, following the quantitative experiments recorded in Part I,[1] and continued until the middle of the following December. During this time only five quantitative experiments were made and these have been included with the earlier measurements. The qualitative experiments consisted in making silver deposits under varying conditions in small voltameters, which could be easily examined under the microscope or photographed. In addition to these we made some deposits in the field of a microscope and investigated the potential relations between anode and cathode. After resuming the quantitative work we still made a few qualitative tests from time to time and have included them here. In Section II of this paper some further qualitative work will be described in connection with the chemistry of the filter paper voltameter.

1. JUSTIFICATION OF THE QUALITATIVE METHOD

From the first experiment in which we used the porous pot we have been impressed with the difference in appearance between deposits made when filter paper is present and when it is not. As the work progressed we found the appearance under a binocular microscope so reliable a criterion for the presence of such impurities as considerably affect the weight of deposit that we felt justified in hastening the work by making qualitative instead of quantitative experiments in order to test the effect of a large number of impurities. These were added to pure silver nitrate solution in the hope of throwing light on the chemical or mechanical processes by which filter paper and kindred substances not only modify the crystalline structure of the deposited silver, but also appreciably increase its weight.

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[1] This Bulletin, 9, p. 151.

Although the appearance to the eye of the deposit may change with the depth of deposit, the appearance of the deposit under the microscope indicates whether it has come down from an electrolyte containing filter paper, or the products of filter paper, or certain other organic impurities, or whether it has come down from a pure electrolyte of $AgNO_3$ and water uncontaminated by such foreign substances. In the first case the deposit is noncrystalline or imperfectly crystalline, according to the quantity of the impurity. It may resemble molten metal that has been dropped on a cold plate and spattered, or lava having a rough, irregular surface, and the deposit more or less massed together; or it may be in needle-shaped crystals, or imperfectly crystalline when the impurity is slight. The color may be grayish when relatively large quantities of impurities are present, or merely tarnished when very small quantities are present. The pure electrolyte in a Richards or Poggendorff voltameter[3] gives a beautiful crystalline deposit, the crystals having well-defined faces and angles, and looking much like glass or diamonds under the microscope, as they are generally without a metallic luster. In the larger cups (with one-half ampere for two hours) the crystals are well separated, the clean platinum surface showing between the crystals. In the smallest cups, where the quantity of silver is twice as much per unit of area, the crystals are elongated, but otherwise similar.

2. APPARATUS EMPLOYED

The results of most of the qualitative experiments are most easily presented by showing the photographs of the deposits obtained. These photographs were made by means of a vertical camera and microscope for the more highly magnified (5 to 16 times). For the smaller magnifications an ordinary camera, with bellows extended, and a symmetrical lens was generally used.

Many of the qualitative runs were made in two small platinum dishes 4 cm in diameter by 1.5 cm deep, having approximately 25 sq cm surface. As the large cups ordinarily used had seven times this area, the current through the small voltameters was made correspondingly small, the current density and time remaining the same.

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[3] These and other forms of voltameter are described in Part I of this series of papers.

3. STANDARD TYPES OF DEPOSIT

As we have before stated, the difference between the deposits made in the Rayleigh and Richards voltameters is very striking and is shown in the following photographs:

Fig. 1 shows some of the deposit removed from a normal Rayleigh voltameter of large size, having one sheet of filter paper to separate the anode and cathode, while Fig. 2 shows five striations stripped from the sides of a dish in which the electrolyte had been contaminated with an excess of filter paper. These are to be contrasted with Fig. 3, which is from a normal Richards voltameter, large size, and Fig. 4 from a normal Richards, small size, and Fig. 5 from a Poggendorff voltameter. Considering these as standard types of deposit we now turn to the tests made in a qualitative way only.

B. FILTER PAPER EFFECT

1. ACTION OF WATER UPON FILTER PAPER

In the investigation of the action of filter paper on silver nitrate we were led to inquire whether it was essential that the filter paper should come in contact with the silver nitrate itself or whether it was sufficient to immerse the paper in water subsequently used for making the $AgNO_3$ solution. This was tried in several ways. A 15 per cent solution of $AgNO_3$ was prepared from 300 cc of double-distilled water in which about 6 grams of No. 595 S & S filter paper had soaked over night. The deposit was strongly striated, indicating an action between filter paper and water. The bottom of the platinum cup with this deposit is shown in Fig. 6. The water used in this experiment after being drawn off from the filter paper was filtered through one sheet of the same kind of filter paper to free it from suspended matter. On adding the silver-nitrate crystals to it a slight bluish tinge was noted. This gradually turned to a reddish brown, suggestive of a colloidal solution. After standing some hours this finely divided substance coagulated and settled to the bottom, leaving the liquid again clear. This experiment was repeated several times with like results.

Fig. 1.—*Deposit removed from a normal Rayleigh voltameter.* × 16

Fig. 2.—*Striations stripped from the sides of a voltameter having electrolyte contaminated with an excess of filter paper.* × 16

Fig. 3.—*Crystalline deposit from Richards voltameter, large size.* × 16

Fig. 4.—*Crystalline deposit from Richards voltameter, small size.* × 16

Fig. 5.—*Crystalline deposit from Poggendorff voltameter.* × 16

Fig. 6.—*Star in bottom of bowl due to contaminated electrolyte.* × 8

Fig. 7.—*Striated deposit from contaminated electrolyte. 10 g of No. 590 filter paper stood in 300 cc of water used for making the electrolyte. For comparison with Fig. 8.* × 1.5

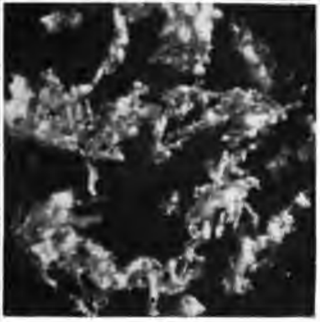
Fig. 8.—*Striated deposit made under same circumstances as in Fig. 7, except that No. 595 filter paper was used, showing that striations are not due to the quality of the paper.* × 1.5

Fig. 9.—*Deposit from a solution contaminated with thoroughly washed filter paper.* × 16

Fig. 10.—*Deposit from an electrolyte contaminated with writing paper.* × 16

Fig. 11.—*Deposit from an electrolyte contaminated with blotting paper.* × 16

Fig. 12.—*Deposit from an electrolyte contaminated with rag paper.* × 16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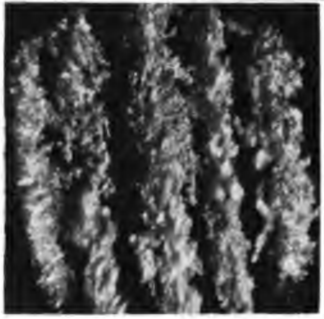
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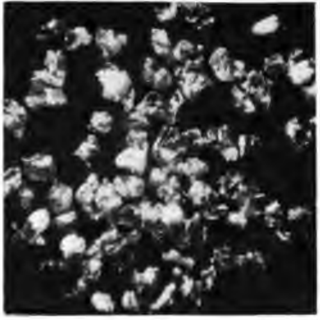
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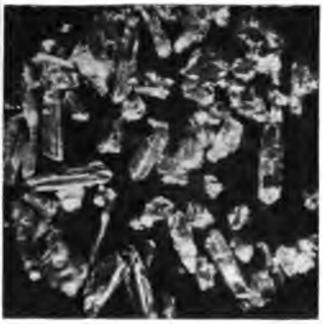
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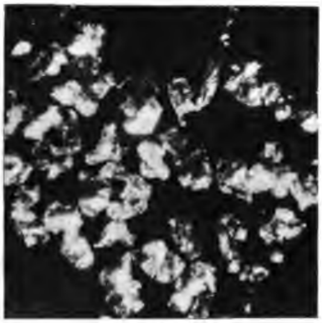
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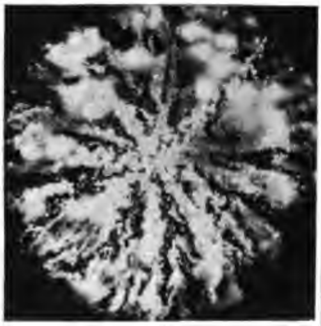
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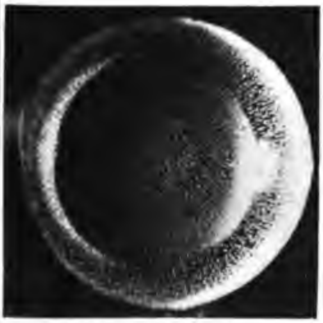
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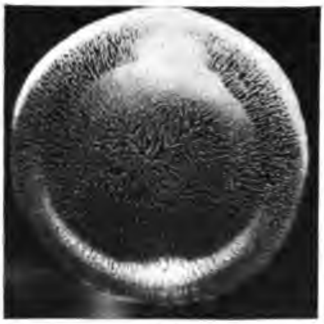
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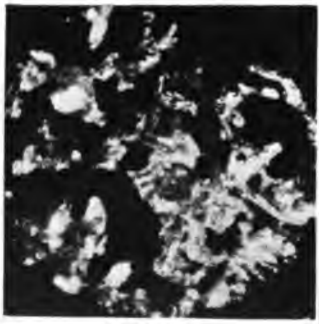
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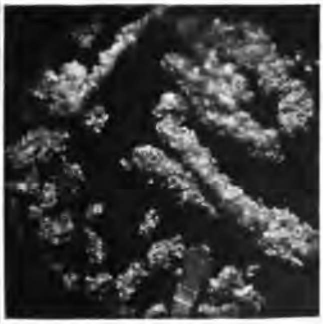
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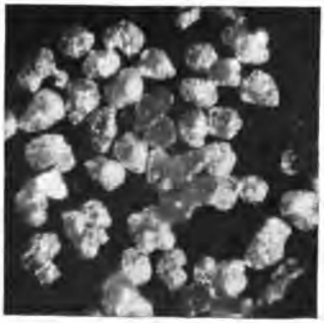
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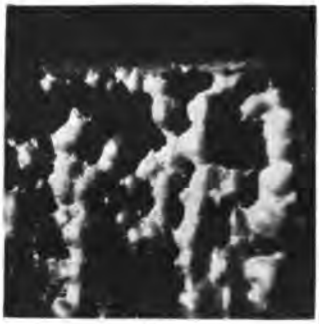
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2. COMPARISON OF DIFFERENT GRADES OF FILTER PAPER

It seemed of interest to determine whether different grades of filter paper produced sensibly equal effects upon the deposit. To test this point, two 10-g samples of No. 595 S & S and No. 590 S & S were weighed out and each put to soak in 300 cc of double-distilled water. On the following day these were used to make up two 15 per cent solutions of $AgNO_3$ for use in the small platinum dishes. These two voltameters were run simultaneously, and except for the chance configuration on the bottom of the cups the two deposits are identical. They are shown photographically in Figs. 7 and 8. As No. 590 filter paper is a higher grade than No. 595 it seems that the effect is the same regardless of the kind of paper, provided the relative amounts of paper to solution are the same, a fact which had been found already in our previous quantitative work.

3. EFFECT OF WASHING THE FILTER PAPER

Prolonged soaking of filter paper in cold distilled water did not apparently lessen its power to react with water or silver nitrate, and thus to alter the deposit. A sample of filter paper which had been repeatedly washed during the preceding 12 days was placed in distilled water for some hours and then poured off. This water was then used to make up a 15 per cent solution of $AgNO_3$. The deposit from this was not strongly striated, but was very loose and not distinctly crystalline as from an uncontaminated solution. It is shown in Fig. 9.

4. TESTS WITH OTHER KINDS OF PAPER

On trying other kinds of paper than filter paper we again found the deposit greatly altered although not always in the same way. Fig. 10 shows the result of soaking common writing paper in silver nitrate solution and Fig. 11 the result of white blotting paper. A sample of all-rag paper with sizing produced a very remarkable deposit shown in Fig. 12. The electrolyte for this last was brownish even after filtering, and the deposit was laid down in rounded heads, with here and there a blossom of crystallized silver.

An examination of various samples of filter paper showed that they were made from linen and cotton rags.

Hence, in order to learn which of these substances was producing the effect on the silver nitrate, Mr. W. S. Lewis, of this bureau, kindly prepared for us three sheets of unsized paper, one made exclusively from cotton rag, one from linen rag, and one from wood pulp. These were used in place of filter paper in a quantitative experiment on August 26, 1909. The weights of these papers compared with the weight of a sheet of the same size of No. 595 S & S are as follows:

TABLE I

	Grams
No. 595 S & S	1.90
Cotton paper	1.63
Linen paper	1.04
Wood paper	2.11

The cotton and linen papers were thin and tough, but the wood paper was thick and so easily torn that in dismantling the voltameter after the run the bag broke and precipitated the anode slime down on the deposit, so that the weight could not be ascertained. All the deposits were striated, particularly that from the wood paper, and we believe this deposit would have been found to be much the heaviest if it could have been weighed. The heaviest of the other deposits was from the linen paper. This showed about 30 parts in 100 000 excess over the two standard Richards voltameters that were included in the same run. The deposit from the cotton paper showed only 17 parts in 100 000 excess.

5. EFFECT OF PINE-WOOD SHAVINGS

Several experiments with pine-wood shavings were made and these showed very great changes in the deposit from electrolyte contaminated with it. When the wood was soaked in the electrolyte itself we obtained the deposits shown in Figs. 13 and 14. Even thoroughly washed wood soaked for a short time in water subsequently used for making up the electrolyte showed a marked effect on the deposit, as appears in Fig. 15.

C. ADDITION OF CERTAIN OTHER SUBSTANCES TO SILVER NITRATE

1. ACID

The addition of acid to $AgNO_3$ solutions even in small amounts reduces the size of the crystals with consequent increase in the number. So far as we have observed the crystalline structure of the deposit is not altered if the electrolyte does not contain organic impurities.

The crystals resulting from the addition of 0.15 per cent of nitric acid are shown (Fig. 16). At a later date we investigated the increase in the number of crystals as the acid was added in successive portions. For this purpose a small piece of platinum ruled in squares 0.2 mm on a side was used as cathode in a pure 15 per cent solution of $AgNO_3$ to which we added tenth normal acid a few drops at a time. The number of crystals in any square were counted under a microscope. For each observation four squares chosen at random were counted and averaged. After being counted the deposit was removed from the cathode, which was then washed and made ready for the next deposit. The experimental difficulties are very great because the surface conditions of the platinum exercised so pronounced an effect upon the deposit. We maintained these conditions as nearly constant as possible and found increasing numbers of crystals as the acid was added. Twenty-three one-thousandths per cent of acid about doubled the number observed from the same solution when neutral.

2. COPPER SALTS, SILVER ACETATE, ALKALI, COLLOIDAL SILVER, ETC.

In the same manner as above we added small quantities of copper nitrate, which increased the number of silver crystals deposited. But the greatest effect was produced by silver acetate, which increased the number of crystals about 100 times when the silver nitrate was saturated with the acetate. On the other hand, the addition of sodium hydroxide, colloidal solutions prepared by Bredig's method and the extract of filter paper produced no appreciable change in the number of crystals, although modifying their crystalline structure. There is no apparent connection between these effects on the number of crystals and the resulting electrochemical equivalent from solutions containing these substances as impurities. Thus we know from our quantitative

Fig. 13.—*Deposit from an electrolyte contaminated with wood fiber.* × 16

Fig. 14.—*Star in bottom of bowl due to contamination of electrolyte with wood fiber.* × 5

Fig. 15.—*Deposit from an electrolyte contaminated with thoroughly washed wood fiber.* × 16

Fig. 16.—*Deposit showing the small crystals resulting from the addition of acid to the electrolyte.* × 16

Fig. 17.—*Deposit from an electrolyte contaminated with gelatine.* × 5

Fig. 18.—*Same more highly magnified.* × 16

Fig. 19.—*Striated deposit from contaminated solution for comparison with Fig. 20*

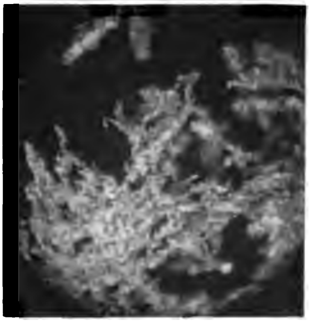
Fig. 20.—*Same electrolyte as for Fig. 19 filtered through a porous cup. Striations eliminated*

Fig. 21.—*Crystalline deposit showing absence of effect of the added silver nitrite.* × 16

Fig. 22.—*Striated deposit due to dextrose*

Fig. 23.—*Same as Fig. 22, but more highly magnified.* × 16

Fig. 24.—*Noncrystalline, deposit due to phloroglucinol.* × 16



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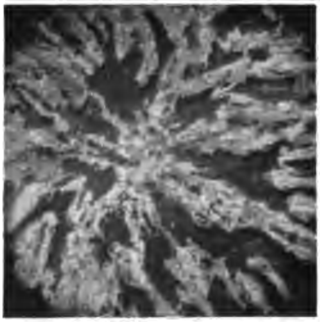

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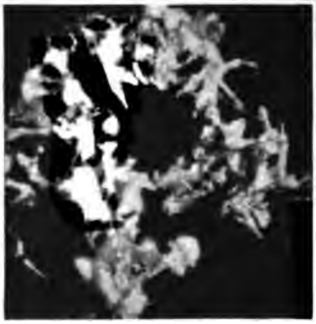

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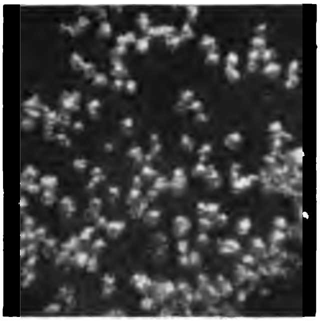

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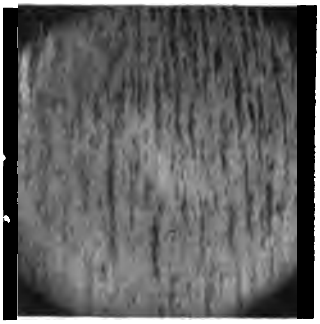

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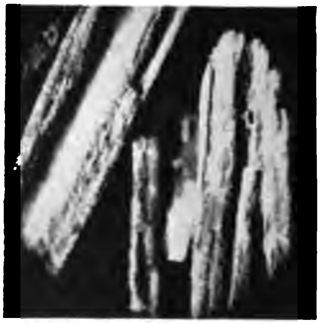

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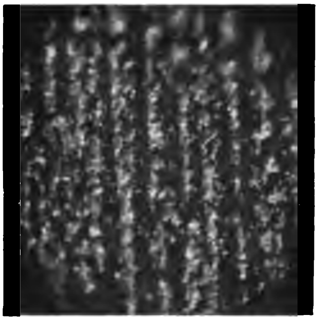

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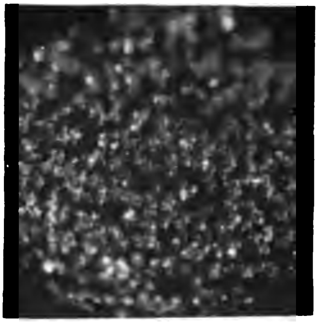

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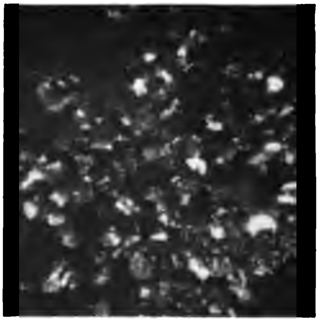

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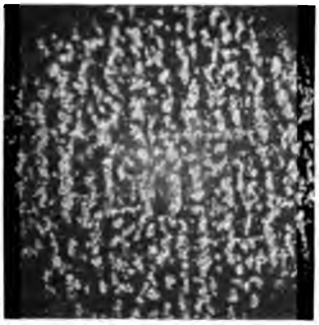

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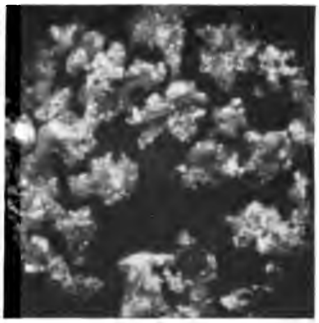

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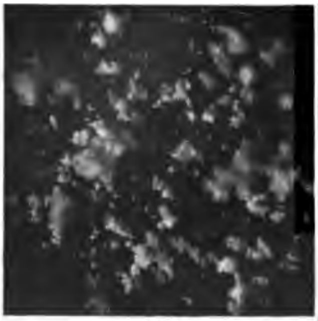

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experiments that the presence of nitric acid causes a reduction in deposit made from very pure solutions as well as increasing the number of crystals, but silver acetate gives an increased weight of deposit. Sodium hydroxide and filter paper extracts cause large increases in the weight of deposit, but appear to be without effect on the number of crystals.

3. GELATINE

Gelatine is one of the "addition agents" occasionally employed in electroplating and is recommended by Betts & Kern [3] for *preventing* crystallization of the deposit in the lead voltameter which they propose as a means of measuring current. We added 1 part in 2000 of pure soluble gelatine to a 15 per cent solution of silver nitrate and electrolyzed it in a small voltameter. The resulting deposit looked more like lead than silver. The striations were very prominent and from the bottom feather-like projections over a centimeter long grew up toward the anode. The deposit to the naked eye appeared amorphous, but under the microscope is was seen to be made up of very small crystals without any regular arrangement. The electrolyte in the mean time turned a bright straw yellow changing to a deep red. This we believe due to colloidal silver thrown out of the solution as a result of the gelatine, but this will be more fully discussed further on in this paper. Samples of the deposit are shown in Figs. 17 and 18.

D. COLLOIDAL SOLUTIONS

1. MIGRATION OF THE COLLOID

By Bredig's method we prepared a considerable quantity of colloidal silver. At first this was a neutral color which slowly turned greenish until at the end of almost a year it is about the color of olive oil. A similar solution of colloidal gold prepared at the same time, which was almost black at first, is now purple.

A U tube 1 square centimeter in cross section and 20 centimeters axial length was filled with the colloidal silver solution and electrodes of platinum foil were fixed in the two ends of the tube. With 120 volts a current of 0.00006 ampere could be passed through it. Clouds appeared in the colloidal solution soon after starting the current and a little gas on the anode. After 20 minutes the color of the solution around the anode was paler than around the cathode, but to make certain that the colloid was actually traveling with the current we reversed the polarity and allowed the current to flow during the night. In the morning the liquid was clear and all the colloid was hanging loosely on the cathode while bubbles of gas were on the anode. When the deposit was heated it turned white like silver, and this was dissolved in HNO_3 and then precipitated as silver chloride to establish the identity of the deposit. The important fact for our present work is that the colloid was carried with the current. On this point there has been some difference of testimony among investigators.[4]

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[3] The Lead Voltameter, Electrician; 54, p. 16, 1904.

We added a small amount of the same colloidal solution to some of the best 15 per cent silver nitrate solution and electrolyzed it. Although there were no striations resulting, the crystalline structure was modified. What are usually single crystals in a deposit made under normal conditions were now aggregates of many small crystals. This we think may be explained by supposing that the colloidal particles as they are laid down become nuclei on which the silver precipitated from the electrolyte itself, grows. This fact also is important and will be taken up again in Section III describing the formation of striations.

2. FILTERED SOLUTIONS

We filtered some of the colloidal solution through a filter made from one of the porous cups as used in the voltameter, employing a vacuum to hasten the filtering. The liquid after passing through the filter was colorless and could only be distinguished from distilled water by a very slightly higher conductivity. This complete elimination of the colloidal silver suggested the possibility of purifying a contaminated solution of $AgNO_3$ by the same process, particularly since in deposit No. 66 we had placed a quantity of filter paper inside the porous cup without producing any apparent effect on the silver deposited outside.

To make a rigid test we prepared a solution of $AgNO_3$ in which filter paper had been soaked over night to insure very marked striations. The electrolyte was then divided into two equal portions, one of which was filtered through the porous cup. The two portions were electrolyzed in two small voltameters in series and identical in every respect except the electrolyte. As one would expect, the unfiltered portions gave *very heavy striations and a decided yellowish deposit.* The filtered portion, on the other hand, gave a deposit that was crystalline, *entirely free from striations, and white.* These are shown in Figs. 19 and 20.

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[4] Allgemeine chemie der Kolloide, Müller, p. 43, 1907.

Because of the importance of this point we made a further test as follows: A strip of platinum serving as a cathode was placed inside a porous cup partly filled with pure silver nitrate. Outside the porous cup was a badly contaminated solution and anode contained in a beaker. In order that the diffusion through the pot should be with the current—that is, from the impure solution into the pure electrolyte—the liquid was made to stand about 1 centimeter higher outside than inside the porous pot. At the end of one hour the deposit was examined under a microscope and found to be good, without any suggestion of filter paper contamination. To make the experiment complete we then put the pure solution outside the porous cup and the impure electrolyte inside under the same conditions as before and obtained a deposit characteristic of filter paper. Because of these experiments we believe the porous cup a very efficient separator between anode and cathode without introducing considerable resistance or other difficulties. As we have used the Richards voltameter we find its resistance about 2 ohms. We have found the resistance of the small Richards voltameter to be from 1.7 to 2.0 ohms, while a voltameter of the same size but without the porous cup showed 1.2 ohms. The resistance of the large size Richards voltameter as used in our early work with a large anode is 0.8 ohm as compared with 0.34 ohm for the same without the porous cup. In our later work we have used small anodes in the large dishes and find the resistance about 1.7 ohms with the porous pot. All the values given are for 15 per cent silver nitrate solution.

E. EFFECT OF OXYGEN AND HYDROGEN IN THE PLATINUM CATHODE

One further qualitative experiment remains to be discussed, and that is an investigation on the effect of gases in the platinum cathode. A part of a strip of platinum was oxygenized by electrolysis in dilute sulphuric acid, and then another part of it was hydrogenized by the same method. When the whole was immersed in silver nitrate and a deposit of silver made on it we found *a large number of small crystals* where the hydrogen had been applied and *a small number of large crystals* where the *oxygen* had been applied to the cathode. We also arrived at the same result during the course of some single potential measurements.

The significance of this result will appear more fully in connection with the discussion of the cause of striations.

II. CHEMISTRY OF THE FILTER PAPER VOLTAMETER

A. ASSUMED INACTIVITY OF FILTER PAPER IN THE VOLTAMETER

1. HISTORICAL

It is evident from the long-continued use of filter paper in the silver voltameter that investigators generally have assumed that filter paper is without appreciable chemical action upon silver nitrate solutions, or at least that the effect of any such action is negligible in the silver voltameter. This assumption seems quite natural when one reflects that filter paper is composed of very pure cellulose, a substance which possesses an extraordinary degree of resistance to the action of most chemical reagents.

Filter paper is first specifically mentioned as a septum in the silver voltameter in the classical work of Lord Rayleigh and Mrs. Sidgwick in 1884.[5] Since that time it has been quite generally used by numerous investigators.[6]

T. W. Richards and his co-workers in 1899 discarded filter paper as a septum and substituted a porous pot in its place. So far as they state, this substitution was not made because of any supposed chemical action of the filter paper upon the electrolyte, but because they desired a septum which would more effectually prevent certain anomalous products, which they supposed were formed at the anode, from reaching the cathode. Indeed, in one experiment, to show the "gain in weight of silver in contact with anode solution" they wrapped the anode of the voltameter from which the anode solution was obtained with filter paper "to retain the fine crystal powder which always separates from it." It is evident from this that they did not suspect any chemical action of the filter paper upon the electrolyte which might affect the result of these tests.

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[5] F. Kohlrausch (1873) merely states that he wrapped the anode in thin material ("zeug"), which probably refers to a textile material.

[6] Kahle; Leduc; Roger and Watson; Smith, Mather, and Lowry; Laporte; and others.

Mylius,[7] at the Physikalisch-Technische Reichsanstalt, stated in 1902 that filter paper reacts on silver nitrate and that this might be a source of error. Guthe[8] (1904) states that for this reason he avoided the use of filter paper in the preparation of his solutions of silver nitrate. Carhart, Willard, and Henderson (1906)[9] observed that some kinds of filter paper, at any rate, gave the deposited silver a faint yellowish tinge and attributed this to impurities in the paper. "We raise the question," they add, "whether the effect of the filter paper itself on the amount of the deposit has been sufficiently investigated."

Smith, Mather, and Lowry (1907)[10] in their elaborate investigation observed an increase of weight of the deposit when the silver nitrate was filtered hot through filter paper, and also when a large quantity of filter paper was used in the voltameter. They noted further that the deposit in such cases was striated, whereas under normal conditions it was not. However, they believed that as ordinarily used the effect of filter paper in the voltameter was negligible and used it throughout their own work.

Since the higher grades of "ash free" filter paper consist of the purest known form of cellulose, the question of chemical reaction between filter paper and the electrolyte resolves itself into one which has to do mainly with the chemical action of water or of an aqueous solution of silver nitrate upon cellulose.

A very brief summary of the current views regarding the constitution and chemical properties of cellulose is perhaps not inappropriate at this point. These views furnished a working hypothesis in our efforts to discover what possible reactions might take place between filter paper and silver nitrate solutions, and furthermore they probably account for the assumption that filter paper must be inert in the voltameter. No attempt will be made to give a thorough or critical discussion of these views, but merely an outline of the more salient points of the generally current theory of the chemical constitution of cellulose will be presented.

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[7] Zs. f. Instrk, **22**, p. 155.

[8] This Bulletin, **1**, p. 21, 1904; Phys. Rev., **19**, p. 138.

[9] Trans. Amer. Elec. Ch. Soc., **9**, p. 375.

[10] Phil. Trans., **207**, p. 545; 1908.

2. OUTLINE OF THE CHEMICAL CONSTITUTION AND PROPERTIES OF CELLULOSE

Cellulose is generally regarded as a polyose of very high molecular weight,[11] i. e., its molecule is composed of a very large number of molecules of a monose or simple sugar (dextrose in the case of cellulose from cotton, etc.) combined with each other (with the elimination of water), so that its formula may be represented thus:

$$n(C_6H_{12}O_6) - (n-1)(H_2O)$$

or, with close approximation by the simpler formula $(C_6H_{10}O_5)n$, since n is a very large number of unknown magnitude and $n-1$ differs from n therefore by an inappreciable amount.[12] In this sense cellulose may be regarded as an anhydride of dextrose. This view is based mainly on the percentage composition of cellulose and the fact that dextrose is formed by the hydrolysis of cellulose, thus:

$$\underset{\text{cellulose}}{(C_6H_{10}O_5)n} + nH_2O = \underset{\text{dextrose}}{n(C_6H_{12}O_6)}$$

The reaction expressed in the above equation takes place in successive steps by the gradual interaction of water (hydration and hydrolysis) and cellulose under the influence of certain hydrolyzing or hydrating agents.

The complete hydrolysis to dextrose is difficult to attain, requiring a quite drastic chemical treatment of the cellulose. The successive steps by which this reaction takes place (due to the increasing amounts of water which combine with the cellulose) give rise to intermediate cellulose-water compounds with elementary percentage compositions varying between that of cellulose on the one hand and of dextrose on the other. When the amount of water which enters into the reaction is relatively small, so that the percentage composition differs only slightly from that of cellulose itself, the cellulose-water compounds are generally referred to as cellulose hydrates, and the process is generally termed hydration. On the other hand, when the amount of water entering into the reaction is relatively large, so that the percentage composition is quite appreciably different from that of cellulose, the process is generally referred to as hydrolysis, a decomposition of the cellulose into products of lower molecular weight in this case being assumed. However, in the literature on cellulose the terms hydrolysis and hydration have often been used interchangeably, notwithstanding the well-known distinction between these terms as ordinarily used with reference to the reaction of substances with water.

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[11] Holleman: Text Book of Organic Chemistry, 1902, p. 287.

[12] Since the atoms of the first molecule of water are split off from two molecules of the monose (or condensation products), the total number of molecules of water thus split off must be one less than the total number of dextrose molecules.

The following general facts are of fundamental importance in this connection:

The extent of the hydration or hydrolysis of cellulose depends upon the intensity of the hydrating or hydrolytic treatment used.[13] The drastic hydrolyzing agents, such as strong acids at high temperatures, give rise to products which approach more or less closely to dextrose in percentage composition and molecular weight, while weaker hydrating agents produce cellulose hydrates differing only slightly in percentage composition from cellulose itself.

The chemical reactivity in general of the products of hydration or hydrolysis is directly dependent upon the extent of their hydration or hydrolysis.[13]

The members nearest cellulose in percentage composition differ only very slightly in their properties from cellulose itself—chiefly in their greater capacity for holding hygroscopic moisture. As the degree of hydration or hydrolysis increases, however, the products become gradually more reactive, as exhibited by their behavior toward special solvents, the greater ease with which they form esters, etc., and in the lower members of the series (i. e., those nearest dextrose in percentage composition and molecular weight) by the gradual increase in their reducing properties.

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[13] Cellulose, Cross and Bevan, Longmans & Co., 1903, p. 5 et seq.; ibid. pp. 20–21.

This gradual development of reducing properties in the lower members of the series finds its explanation in the manner in which dextrose molecules are supposed to be linked together in cellulose or hydrated cellulose. According to this view the linking together of the dextrose molecules is accomplished through the medium of the CO group, to which the strongly reducing character of dextrose is ascribed. The exact mechanism of this linking need not be discussed here. It should be said, however, that in the combination (or condensation) of the dextrose molecules the CO groups are destroyed as such through their interaction with hydroxyl groups, water being eliminated in the process. Consequently, the molecules formed by this condensation are devoid of reducing properties, provided, of course, all the CO groups of the dextrose molecules have thus entered into reaction.

In the hydrolysis of the lower members of the cellulose-water compounds, these CO groups are successively liberated, giving rise to the gradual increase in the reducing properties of the products.

It should be borne in mind, however, that it is only in the comparatively recent work upon cellulose that it has been recognized that even these more completely hydrolyzed cellulose-water compounds possess reducing properties characteristic of the CO group.[14]

In the formation of cellulose-water compounds containing relatively less amounts of combined water than those just discussed, the addition of water does not bring about decomposition in the sense that CO groups are liberated. In such cases, if actual hydrolysis has occurred the inference is that the linking together of the proximate constituents of the molecule has taken place between hydroxyl groups only, so that no CO groups are involved, and consequently these are not liberated by the hydrolysis.

The less completely hydrolyzed products and of course the merely hydrated celluloses are quite generally regarded as nonreducing carbohydrates, i. e., they show no reduction of Fehling's solution nor any other reactions indicating the presence of free CO groups. Indeed, as we have already stated, the hydrated celluloses at least are said to differ from cellulose itself only in respect to what are considered to be their less essential chemical properties, such, for example, as their varying resistance to hydrolysis, esterification, or solution in certain special solvents. In general their very close resemblance to cellulose is shown by their negative or nonreactive characteristics.

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[14] See, for example, Vignon, C. R., 126, p. 1355 (1898).

Quite separate from all questions of constitution, the one generalization most emphasized regarding the chemical nature of cellulose is its great resistance toward the action of the most various chemical reagents. It is quite frequently pointed out that this nonreactive character is in fact a necessary consequence of its method of isolation from the woody tissue of plants, inasmuch as cellulose is simply the insoluble residue left after various drastic treatments of the raw material have removed the more reactive impurities with which it is associated.

3. SOME CHEMICAL PROPERTIES OF SILVER NITRATE SOLUTIONS

Remembering what has just been said regarding the chemical nature of cellulose, it becomes apparent why one would not expect a solution of silver nitrate, when pure, to react upon cellulose to an appreciable extent. A solution of pure silver nitrate, even if slightly acid from its own hydrolysis, should possess only exceedingly weak hydrolyzing power upon cellulose, and one would not expect it to have any action at all upon cellulose in the sense of the production of substances having free CO groups, and therefore possessing strong reducing properties. So far as hydrolytic action is concerned, therefore, one would expect at most merely the formation of slightly hydrated modifications of cellulose, which, while being somewhat more soluble than cellulose itself, would otherwise differ only inappreciably from the latter in all their more essential chemical properties.

Furthermore, neutral or acid solutions of silver nitrate are only very slightly reduced even by carbohydrates containing free CO groups. It is for this reason that in the well-known silver-mirror test for aldehydes (or for the free CO group in general) only strongly alkaline ammoniacal silver solutions are employed. On the other hand, polyoses, such as cane sugar, which do not contain this group, do not show the characteristic reduction of even the strongly alkaline ammoniacal silver solutions if the conditions are regulated so as to avoid hydrolysis of the carbohydrate. Since both cellulose and its hydrated modifications are regarded as belonging to this latter class of polyoses, which contain no free CO groups, one would not expect them, when pure, to reduce to any appreciable extent even these strongly alkaline solutions of silver nitrate, much less that they could reduce neutral or slightly acid solutions of silver nitrate, which are much more stable toward reducing agents than are alkaline solutions.

B. EFFECT OF ORGANIC MATERIAL IN THE VOLTAMETER

1. DARKENING OF SILVER NITRATE BY ACTION OF ORGANIC MATERIAL

The statement is frequently made that silver nitrate becomes darkened by the action of "organic substances" under ordinary conditions in the light, the inference of course being that silver nitrate is reduced to finely divided metallic silver, to which the dark color is due. This should not be taken to mean that all organic material of whatever nature can reduce silver nitrate to metallic silver under ordinary conditions.

So far as we are aware no instance has been described where a reduction of pure silver nitrate to metallic silver is brought about by the action of organic substances which are not themselves reducing agents and which are incapable of hydrolytic decomposition into strong reducing agents of some kind.[15] It seemed safe to infer therefore that in most cases where "organic substances" are mentioned in this connection some kind of paper or other textile material is probably meant. In fact, we were unable to detect any darkening either of solutions of pure silver nitrate or of the dry crystals when allowed to remain in contact with paraffin for several days, whereas with paper or silk the darkening always occurred. In accord with this fact it was found that neither paraffin nor the lighter hydrocarbon oils such as hexane and heptane had any effect upon the appearance of the silver deposit when these substances were added to the electrolyte.

We therefore believed almost from the first that notwithstanding the resistant nature of cellulose hydrolytic decomposition probably took place to a very slight extent when silver nitrate was brought in contact with filter paper or similar organic material and that the products thus formed gave rise to the formation of striæ. The excess weight of the silver deposit might be due to silver thrown down by purely chemical action. We therefore added a number of organic substances to the electrolyte to see whether our supposition were true that any hydrolyzable organic material of the nature of cellulose could produce the abnormal, striated deposits of the same character as those which are obtained with filter paper. The results previously obtained with various kinds of paper, wood fiber, linen, etc., had seemed to support this view. (See p. 216.)

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[15] This statement refers to the influence of the organic material itself and not to the action of light alone. Later it will be shown that a solution of pure silver nitrate free from all organic impurities is not appreciably reduced even by the prolonged action of light.

2. EFFECT OF CANE SUGAR AND STARCH IN THE VOLTAMETER

Among the first examples of hydrolyzable organic material whose effects in the voltameter were tried were cane sugar and starch. They were selected because of their very close chemical relationship to cellulose. We were surprised, however, to find that neither of these substances when added to the electrolyte produced any indications of the formation of striated deposits when the solutions were electrolyzed in the voltameter in the usual manner. The solutions electrolyzed contained approximately 1 per cent of each of these substances. The starch used was Kahlbaum's cornstarch. The cane sugar was prepared by Mr. R. F. Jackson, of this bureau, for use as a standard in saccharimetry, and was very pure. There was no darkening of the electrolyte after standing 24 hours, such as is observed if filter-paper extract is present in the electrolyte.

These results showed that the disturbances which give rise to the abnormally heavy, striated deposits are not due to the action of organic material as such, nor even to such organic material as is easily hydrolyzed, but depend in some way upon the specific nature of the organic material used. It was clear that filter paper is more reactive under the conditions present in the voltameter than either cane sugar or starch. This fact is quite out of harmony with the current views regarding the relative reactivities of these substances and suggested the possibility that the activity of the filter paper might possibly be due to the presence in it of impurities of a more reactive nature than cellulose.

C. IMPURITIES IN FILTER PAPER

1. ORGANIC IMPURITIES

The very pronounced effects produced by raw woody fibers (described on p. 216) led us to suspect that if, as suggested above, impurities in the filter paper were producing the disturbing effects they might be resins, pectocelluloses, glucocides, or similar organic impurities which are closely associated with cellulose in plant tissue and which are very difficult to separate completely from the pure cellulose. These impurities are much more reactive than cellulose itself and some of them are very easily decomposed by hydrolysis or decay into strong reducing agents, such as dextrose, phenols, or similar substances.[16] That they are, however, not the cause of these disturbances is shown by experiments described below (p. 231).

2. INORGANIC IMPURITIES

It is well known that even the purest forms of ash-free filter paper contain small amounts of inorganic salts. It appeared possible that these could precipitate insoluble silver salts which in some manner might produce the disturbing effects in the voltameter. Smith and Lowry, indeed, came to the conclusion that insoluble silver salts were responsible for the high values for the electrochemical equivalent obtained with used solutions of silver nitrate. They, however, considered that these impurities resulted chiefly from the action of contaminations in the atmosphere, such as hydrochloric acid and hydrogen sulphide, rather than from the filter paper. They pointed out that many of the so-called insoluble silver salts are soluble to an appreciable extent in relatively concentrated silver nitrate solutions, from which they are precipitated upon dilution, and emphasized the fact that the conditions at the cathode favor such a precipitation, owing to the thin film of dilute solution of silver nitrate which is formed there by the deposition of silver. For example, they obtained high values for the electrochemical equivalent by adding silver chloride or silver sulphide to the electrolyte. In one case, namely, with silver hyponitrite, they actually obtained a deposit which was strongly striated, a result which they attributed to the hyponitrite, although filter paper was used in preparing this salt. They proposed a theory of the formation of striæ based upon these observations.

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[16] Tannin yields the trioxybenzoic acid, gallic acid, and glucose. Coniferin yields dextrose and coniferyl alcohol, which latter is a phenol derivative. The mere decay of protoplasm yields paracresol, which is a very strong reducing agent.

That the effects of filter paper in question can not be due to these inorganic impurities is shown by the experiments described in the following section.

3. SOLUBLE IMPURITIES

In harmony with the idea that striæ are caused by impurities of some kind it had been found early in our work that aqueous extracts of filter paper were quite as effective in producing striated deposits as the sheets of filter paper themselves.

To test the whole matter as to the effect of impurities, whether organic or inorganic, therefore, it was only necessary to extract these impurities as completely as possible and then test the influence of both the extracted filter paper and the extract itself in the voltameter.

The extraction was carried out in a Soxhlet apparatus made entirely of resistent glass to avoid possible contamination from cork or rubber stoppers. The experiment continued for six hours and the heating was regulated so that a complete extraction took place about every half hour. Thus the filter paper was extracted about 12 times with freshly distilled water. This thoroughly extracted filter paper was allowed to remain in the extraction apparatus until comparatively dry, being protected from possible contact with acid or ammonia fumes of the laboratory by means of guard tubes of soda lime and concentrated sulphuric acid connected to the upper outlet of the condenser tube. The boiling flask containing the extract had previously been removed and the lower opening of the condenser and the siphon closed by means of rubber stoppers.

The dry, extracted filter paper was then removed and tested as to its "activity" in the voltameter in the usual manner by noting whether it produced a striated deposit. Contrary to expectations, it was found that if there were any differences at all, the extracted filter paper was even more active than that which had not been treated. Moreover, the active soluble substance evidently accumulated in the water as the extraction continued. The extract was distinctly straw colored and was very much more active in producing striæ when added to the electrolyte than the extract obtained by a single treatment or merely a few such treatments with water.[17]

It was later found that immediately after such an extraction filter paper is comparatively inactive, indicating that on standing a spontaneous change of some kind takes place which results in the paper becoming active again. The nature of this change will be discussed later.[18]

D. PRODUCTION OF ABNORMAL DEPOSITS BY ADDITION OF CERTAIN IMPURITIES

1. GENERAL STATEMENT—HISTORICAL

Having determined that the effects of filter paper in question were not due to the fact that it is of an organic nature merely, nor to the influence of impurities (organic or inorganic) contained in the filter paper, it became of importance next to investigate certain other explanations of the influence of filter paper which the experiments of previous investigators had led us to postulate.

In investigating the nature of the changes occurring in the electrolyte at the anode, Richards and Heimrod [19] state that they obtained reactions showing the presence, among other products, of silver nitrite. They therefore tried the effect of adding silver nitrite to the voltameter and concluded from these results that when perpared from potassium nitrite and silver nitrate this salt had the effect of increasing the mass of the electro-deposited silver by between 30 and 80 parts in 100 000. They do not state whether the deposit was striated, but from our own experience it seemed probable that it must have been. Obviously, filter paper might reduce silver nitrate to nitrite, and thus explain the fact (which we had found) that the abnormalities are due to the filter paper itself, and not to the anode electrolyte. Smith and Lowry (loc. cit.), however, had repeated these tests, using their form of the filter paper voltameter, and had come to the conclusion that the nitrite could have no appreciable influence. We obtained the same result with silver nitrite prepared from potassium nitrite (see Fig. 21). Continuing further in this direction they also tried the effect of adding silver hyponitrite to the electrolyte. They found that when a 20 per cent silver nitrate solution was saturated with silver hyponitrite (prepared from freshly formed potassium hyponitrite made by reducing the nitrite with sodium amalgam) the deposit of silver was abnormally heavy and very strongly striated. This observation led them to suggest that the disturbing effects of filter paper (which they had observed only when large amounts were used) might be due to the formation of silver hyponitrite by the reducing action of the filter paper. They made no tests for the presence of hyponitrite in any of these cases, and in this connection make the following statement: "We do not wish to commit ourselves to the view that hyponitrite is the only or even the main source of the disturbances which have been noticed by ourselves and others." They proposed it merely as a suggestion. Nevertheless this explanation appeared worthy of further investigation, especially since it was the only instance of which we were aware where it had been claimed that the addition of a single definite chemical compound to the electrolyte produced the peculiar striated appearance of the deposit, although there was some uncertainty even in this case as to whether the use of filter paper in preparing the hyponitrite had not vitiated their results.

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[17] Our experience with glass vessels precludes the possibility that the pronounced effects in this case could have been due to the solution of a portion of the glass.

[18] When raw unwashed silk is extracted in like manner the extract, when added to the voltameter, brings about the formation of heavy striated deposits, but the extracted silk, even when allowed to stand, does not become active again in the sense that it produces heavy deposits. If used again it affects the results in the opposite sense, i. e., the deposits are made lighter. With repeated use of the same silk this effect persists, and is accompanied by an increase in the acidity of the electrolyte. This effect also will be discussed more fully.

[19] Proc. Amer. Acad., 37, p. 422.

It was of course difficult to see, on the basis of this explanation, just why other kinds of organic material, especially cane sugar and starch, which are so closely related to cellulose, do not produce the effects in question. It seemed possible, of course, that hyponitrite might be formed by the reducing action of pure cellulose and not by starch or cane sugar; the effects could then be attributed to some peculiar property of hyponitrite not possessed by the reduction products formed in the case of cane sugar or starch. But just why the products should differ so sharply in the two cases, where the chemical relationships of the reducing substances are known to be so close, was of course very difficult even to surmise. It was decided, however, to repeat these experiments of Smith and Lowry in the hope that some additional information might be obtained which would lead to a more definite and satisfactory explanation of the peculiar effects of filter paper.

2. EFFECT OF SILVER HYPONITRITE

In testing the influence of hyponitrite the conditions as described by Smith and Lowry were modified somewhat by using a more dilute solution of silver nitrate (15 per cent) in order to duplicate more nearly the conditions which obtain in the filter-paper voltameter. Such a solution does not dissolve as much silver hyponitrite as one more concentrated, but since strongly striated deposits had been obtained with the more dilute electrolyte, it seemed best to use the same conditions in the test. If the production of striæ were due primarily to silver hyponitrite, a solution of the electrolyte of the same strength as that used in the voltameter completely saturated with respect to hyponitrite should show the effect in a very marked manner. The silver hyponitrite was prepared from Kahlbaum's potassium nitrite. The procedure followed was essentially the same as that described by Hantzsch and Kaufmann.[20] This method yields a pure product especially free from traces of hydrazine and hydroxylamine, which are usually present in silver hyponitrite prepared by reduction of nitrite, unless special care is taken to remove them. The whole process was carried out in a dark room and the material was very carefully protected from contamination of filter paper or other organic material. The salt was spread upon an unglazed porcelain plate and preserved in the dark in a desiccator over sulphuric acid.

The electrolyte was prepared by adding a weighed amount of silver nitrate to a saturated solution of the hyponitrite (free from the solid salt) contained in a brown glass-stoppered bottle. That the electrolyte was saturated with respect to hyponitrite was indicated by the formation of a cloud when the silver nitrate crystals were added. Without waiting for this cloud to settle the solution was immediately electrolyzed in a small voltameter under normal conditions. We were surprised to find that the silver deposit was in all respects similar in appearance to those obtained from pure silver nitrate. There was not the faintest indication of the presence of striæ.

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[20] Ann. d. Chem. u. Physik, **292**, p. 320 (1896).

3. PRODUCTION OF STRIÆ BY THE ADDITION OF HYDRAZINE AND HYDROXYLAMINE TO THE ELECTROLYTE

The effect of hydrazine and hydroxylamine upon the appearance of the silver deposited in the voltameter was tested because of their relationship to nitrous and hyponitrous acid as members of the series of compounds produced by the electrolytic reduction of nitric acid. Also, hydrazine and hydroxylamine are usually present as impurities in silver hyponitrite, unless special care is taken to remove them, and it was thought possible that the formation of striæ in the experiments of Smith and Lowry might have been due to the effect of these impurities rather than to the hyponitrite, since we had found the latter to be inactive.

A series of electrolyses was carried out, therefore, with electrolytes containing about 0.5 per cent by weight of the nitrates of hydrazine and hydroxylamine respectively. The hydrazine and hydroxylamine were added in the form of their hydrochloride salts, the silver chloride thus formed being filtered off through asbestos, leaving these compounds in solution in the form of their nitrate salts. When these solutions were electrolyzed it was found that the silver deposit obtained in each case was distinctly striated.

Until the results just described were obtained the formation of striated deposits had been observed only when some form of natural woody fiber (or silk) had been in contact with the electrolyte. Even substances which are considered to be very closely related chemically to cellulose, such as starch and cane sugar, had failed to produce this very peculiar effect. It was evident, therefore, that a promising clue had been uncovered.[21]

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[21] The fact that these two reduction products of nitric acid were the only definite chemical compounds tried so far which possessed the peculiar property of producing striated silver deposits seemed in itself

4. PRODUCTION OF STRIÆ BY THE ADDITION OF STRONG REDUCING AGENTS TO THE ELECTROLYTE

Many experiments were carried out in the attempt to discover in what manner hydrazine and hydroxylamine produce striæ. It was finally concluded that the strongly reducing character of these substances was the essential condition. To test this hypothesis a large number of strong reducing agents, mostly aldehydes and phenols, were separately added to the electrolyte and their effect upon the appearance, and in some cases upon the mass, of the deposit was carefully noted. Among those tried were the following: Dextrose, invert sugar, formaldehyde, acetaldehyde, furfuraldehyde, benzaldehyde, phenol, resorcinol, hydroquinone, and phloroglucinol. Approximately 1 per cent of the reducing agent was added in each case.

The electro-deposited silver obtained from electrolytes containing in each case one of these reducing agents was carefully examined, both as to its general appearance (whether striated and to what extent) and also as to the appearance of the silver crystals under the microscope. A few photographs of these silver deposits were made and are shown in Figs. 22 to 25. The deposits were striated in all cases, the more marked effects in general being produced by the stronger reducing agents of the group.

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sufficient to warrant a careful search being made for their presence in silver nitrate solutions contaminated with filter paper.

In the present instance the more commonly used tests with permanganate or other strong oxidizing agents could not be used on account of the presence of oxidizable organic material, and on the other hand the less vigorous oxidizing agents, such as Fehling's solution and mercuric chloride, were not considered sufficiently characteristic for the case in hand. In other words, none of the tests which depend upon the reducing properties of these substances could be used. Tests of a more characteristic nature were desirable. For hydroxylamine, the test of Bamberger (Ber., **32**, p. 1803, (1899)) was found to be the most satisfactory for our purpose; Angeli's (Gazz. Chim. Ital., **23**, p. 101, (1893)) test with nitroprussiate is not so easily controlled and is less sensitive than the former. (See also L. J. Simon, C. R., **137**, p. 986, (1903)).

It was found possible by means of this test to detect with certainty as little as one part of hydroxylamine hydrochloride added to 100 000 parts of water or aqueous filter paper extract. We were unable, however, to detect the presence of even the slightest trace of hydroxylamine either in concentrated filter paper extracts which had been acidified with varying amounts of nitric acid or in silver nitrate solutions contaminated with filter paper. In the latter case before making the test the silver was completely precipitated as chloride with potassium chloride solution and the precipitate removed by filtering the solution through asbestos.

In testing for hydrazine we employed its property of forming the very insoluble benzalazine when treated with benzaldehyde in acid or alkaline solution. This test was first used by Curtius and Jay (Ber., **22**, p. 134 (1889)), but they make no statement as to its sensitiveness in detecting minute traces of hydrazine. We found that it is possible to detect by this means a few parts of hydrazine hydrochloride in 100 000 of solution. Examination of numerous concentrated extracts of filter paper to which either nitric acid or silver nitrate had been added and which were allowed to stand for varying lengths of time gave no evidence of the presence of hydrazine, although 0.005 per cent of hydrazine hydrochloride when added to such aqueous filter paper extracts could be detected easily.

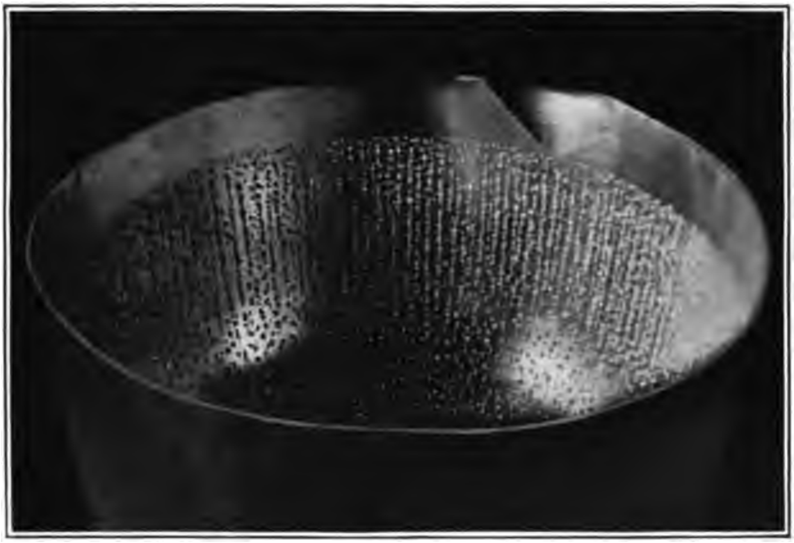

Fig. 25.—*Striated deposit caused by the addition of polymerized furfuraldehyde to the electrolyte*

It has been pointed out already that such mild reducing agents as starch and cane sugar are without appreciable influence upon the appearance of the electro-deposited silver. It would appear, therefore, from the similarity in the effects upon the silver deposit of filter paper, on the one hand, and of these very strong reducing agents, on the other, that the filter paper actually functions as a very strong reducing agent, much stronger than either cane sugar or starch. Also, the extraction experiments already described show that this action in the voltameter can not be due to impurities, but must be attributed to the cellulose itself. It became of importance, therefore, to carefully examine the products formed by the interaction of these cellulose extracts with silver nitrate in order to determine whether the action is one of actual reduction, as the above results so strongly indicate, and especially to determine whether metallic silver is actually formed by the reaction and to compare the results in this case with the action of cane sugar or starch under the same conditions. As a problem of secondary importance in its relation to the voltameter, but of even greater import in other respects, it was of interest to determine in what way cellulose could thus function as a much stronger reducing agent than either starch or cane sugar. These questions we shall discuss in the subsequent sections.

E. REDUCTION OF SILVER NITRATE TO METALLIC SILVER BY FILTER PAPER EXTRACTS—COLLOIDAL SILVER

1. PREPARATION OF CONCENTRATED SILVER HYDROSOLS BY MEANS OF FILTER PAPER EXTRACT

In studying the reaction between silver nitrate and cellulose, those constituents of the cellulose which have the greatest effect in the voltameter were concentrated. This was done for two reasons. First, it was desired to study only that reaction, of several possible concomitant ones, which was responsible for the particular effects in question of filter paper in the voltameter. In the second place, it was desired to obtain as much of the products of the reaction as possible, so that their properties could be more readily examined and their nature determined. This concentration of the active material was effected by extracting a given mass of filter paper with the smallest volume of water practicable, repeating the extraction several times with the same portion of water until no more material seemed to be extracted, as judged by the activity of the extract in the voltameter. This usually required about three or four extractions. Later it was found that the active material could be further concentrated by evaporation; but since a portion of the active material volatilized with the steam, it was decided to make the tests upon the extract as obtained, so as not to depart in the least from the conditions which actually obtain in the voltameter. If the extracts are evaporated to dryness on the steam bath, an amorphous, slightly brown residue is left which volatilizes completely upon ignition in the bunsen flame. (A single extraction of 50 grams of filter paper with 300 cc of distilled water at 35° C for 15 minutes yielded approximately 75 milligrams of residue when evaporated to dryness on the steam bath; by repeating the extraction, extracts of greater concentration have been obtained.) When one-half per cent of silver nitrate is added to such extracts the slightly straw-colored liquid gradually assumes a deep red wine color which begins to develop in from 10 to 15 minutes. The resulting solution appears perfectly homogeneous to the eye and can be filtered through ordinary filter paper without any visible change in its appearance. This solution is practically permanent without further treatment. In one case no change was noticed after standing two months in a glass-stoppered bottle; after five months a dark red-brown sediment had collected at the bottom and a faint metallic mirrorlike film had formed underneath the sediment, although no film was visible on the sides of the bottle. The red color of the solution itself had become somewhat fainter, but was still a deep clear red.

The appearance and properties of these solutions prepared from filter paper extracts are entirely similar to the colloidal silver solutions of Muthmann,[22] Carey Lea,[23] and others,[24] except that the solutions prepared from the concentrated filter paper extracts are if anything still more permanent than those of Muthmann and Lea and even more difficult to coagulate from the mother liquor, as will appear later. When the less concentrated filter paper extracts were used the solution was much less deeply colored, usually having a faint purple to bluish tinge; the sediments formed more quickly and also had a much darker color. This sediment, as well as that from the dark red solutions, consists almost entirely of finely divided metallic silver, as will be shown later on. Solutions of cane sugar of many times the concentration of these cellulose extracts gave no such evidence of the formation of colloidal metallic silver, thus confirming our first inference from their relative activity in the voltameter.[25]

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[22] Ber., **20**, 983 (1887).

[23] Amer. Jour. Sci. (Sill), [3] **37**, 476; **38**, 47; **41**, 482; Chem. N., **50**, 34; **48**, 53; Phil. Mag., [5] **31**, 497.

[24] Schneider, Ber., **25**, 1164 (1892); Prange, Rec. Trav. chim. Pays-Bas, **9**, 121. Lottermoser and Meyer, J. prakt. Chem., **56**, 241.

2. "PROTECTED" AND "UNPROTECTED" COLLOIDAL SILVER; INFLUENCE OF ORGANIC COLLOIDS

The greater permanency of the colloidal solutions prepared from concentrated filter paper extracts and the fact that they are only very slowly coagulated in the presence of the unreduced silver nitrate, which is a strong electrolyte, suggests that the colloidal silver is "held up" by the "protective" action of the organic material in the extract, which is itself a well-defined colloid. (Preliminary examinations of concentrated filter paper extracts made in this laboratory by means of the ultramicroscope show that they exhibit the characteristic appearance of colloidal solutions.) Furthermore, the organic colloids in the extract belong to the class of so-called reversible colloids, if we adopt the restricted and more rational classification of Zsigmondy,[26] for after evaporation even at the temperature of the water bath the residue may again be "redissolved" in water. On the basis of the same classification, colloidal silver solutions prepared by Bredig's method in the absence of other colloids are irreversible.[26] Since, as a general rule, the protective colloids belong to the class of "reversible" colloids,[26] it is seen that we have ideal conditions for the formation of a protected colloidal solution of silver in this case.

As already stated, the colloidal silver coagulates and settles more readily from silver nitrate solutions only slightly contaminated with filter paper extract than from those prepared with concentrated extracts. This indicates that the protective action is dependent upon the amount of cellulose extract present relative to the amount of silver nitrate, and that under actual conditions in the filter paper voltameter the colloidal silver is protected to some extent from the coagulative action of silver nitrate and other electrolytes. This condition may account for the greater effectiveness of filter paper in the voltameter as compared with that of the other strong reducing agents, such as dextrose, formaldehyde, etc., which, although strongly reducing in character, are not protective colloids.

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[25] Further on in this chapter the relative rates of these reactions are given, and this conclusion is thus established in a very definite manner.

[26] Colloids and the Ultramicroscope, Zsigmondy-Alexander; 1902, p. 25 et seq.

Whether the greater effectiveness of "protected" colloidal silver is due to a greater permanency, to a greater concentration, or to some other difference in the properties of the colloidal silver solutions, or whether due in part to the independent action of the protective colloid itself, is a matter about which there may be some question. While the migration experiments described on page 219 show that colloidal silver migrates to the cathode, it is of course possible that the protective colloid itself may migrate to the cathode in exactly the same manner and there bring about entirely similar results as to the production of striations, etc. However, all of the data which we have been able to find indicate that not only cellulose, but practically all other kinds of organic colloids as well, migrate toward the anode.[27] Moreover, since non-reducing organic colloids are "inactive" in the voltameter, and further, since "unprotected" colloidal silver produces similar effects (as shown by the results obtained with the strong reducing agents, such as dextrose, formaldehyde, phloroglucinol, etc., and also with Bredig's colloidal silver), it would seem more probable that the effects are due primarily to the colloidal silver itself and that the greater effectiveness of the "protected" colloid should be attributed to its greater concentration and greater permanency. Undoubtedly some of the organic colloid is dragged along, so to speak, with the colloidal silver and is deposited upon the cathode, but this can hardly constitute more than a small percentage by weight of the total colloid so deposited. In instances where the electrolyte contained unusually large amounts of filter paper extract (colloidal cellulose hydrates, etc.), we have been able actually to separate this included organic colloid from the silver deposit by amalgamating the silver with mercury.

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[27] See Spring, Bull. de l'Acad. roy de Belg. (3), **35**, 780–784, 1898. Larquier des Bancels, C. R., **149**, 316–319; 1909. Also Graf von Schwerin und Farbwerke vorm. Meister, Lucius und Bruning, D. R. P. 124509, 124510, 128085.

In one case a deposit (not weighed) made from an electrolyte containing an unusually large amount of filter paper extract, after thorough washing, was amalgamated with 50 times its mass of mercury and extracted with water. The amorphous cellulose was plainly visible suspended in the water. Its total mass obtained by loss on ignition (after evaporating) was 4.5 milligrams. The total weight of the silver deposit was about 4 grams. Judging from the character of the striæ and general appearance of the deposit it probably was heavier than a normal deposit by not less than one-half of 1 per cent. But, under the usual conditions at least, in the filter paper voltameter, the weight of this included organic material is only a small fraction of the total excess weight of the deposit. This excess appears, therefore, to be due mainly to the colloidal silver alone, since the remainder of the deposit amalgamates completely. In another instance a weighed deposit from an electrolyte contaminated with filter paper, made in a voltameter in series with a standard voltameter, showed an excess weight of about 4 mg. After carefully amalgamating with 50 times its weight of mercury, then extracting the amalgam with very pure water, and evaporating the extract, a residue judged to be organic material was obtained which weighed 0.43 mg, and which showed a loss upon ignition of 0.38 mg. In other words, only about one-tenth of the total excess weight could be attributed to the included organic material liberated in this way.

Other instances of the pronounced effects produced by reducing agents which can function as protective colloids are seen in the effects produced by the addition of gelatin and unwashed raw silk (due to the silk glue), both of which give well-defined colloidal solutions in water and very easily reduce silver nitrate to colloidal silver solutions in a manner similar to that shown by cellulose.

F. PROPERTIES OF COLLOIDAL SILVER PREPARED BY MEANS OF FILTER PAPER EXTRACT

1. COAGULATION OF THE "PROTECTED" COLLOIDAL SILVER BY MEANS OF ALCOHOL

By magnifying the conditions actually present in the filter paper voltameter, i. e., by increasing the proportion of "soluble" cellulose relative to the silver nitrate, it has been possible, as already stated, to prepare permanent colloidal solutions of silver which are not only not coagulated by the silver nitrate present, but which are extremely stable toward all other electrolytes that have been tried. In fact, considerable time was expended in searching for a means of coagulating these concentrated hydrosols so that sufficient hydrogel (coagulated silver) could be collected to enable its properties to be examined. The addition of potassium nitrate in practically all proportions up to saturation had very little effect upon the rate of coagulation. The same was found true of sodium nitrate and ammonium nitrate as well as of the acetates of the alkali metals. Of course, only such salts could be added as do not form an insoluble precipitate with the silver nitrate. Dilute acetic acid brought about partial coagulation on standing two days. Potassium fluoride had no effect when the solutions were kept in platinum.[28]

A highly satisfactory coagulating agent was found in alcohol. When approximately two volumes of alcohol (95 per cent or 98 per cent) are added to one volume of the concentrated silver hydrosol, a dark red sediment begins to form in about an hour, and the solution becomes clear on standing over night. This sediment may be collected on an asbestos filter and washed free from silver nitrate by means of absolute alcohol.

2. PROPERTIES OF THE COAGULATED COLLOIDAL SILVER OR HYDROGEL

(*a*) **Transformation to Ordinary White Silver.**—If a thin film of the silver hydrogel is spread upon a microscope slide, it assumes upon drying a faint greenish tinge by reflected light, but is still a dark reddish brown by transmitted light. When kept at 100° to 110° it gradually assumes a more yellowish tinge by reflected light, finally becoming opaque and having the gray metallic appearance of ordinary finely divided silver. Upon standing several weeks under a bell jar it gradually undergoes the same changes at ordinary room temperatures. This spontaneous change to ordinary gray silver takes place more readily with the darker sediment which settles from the weaker silver hydrosols containing much less filter paper extract than with those just described.

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[28] It would be of interest from the standpoint of the general properties of colloids to remove the silver nitrate completely by dialysis so that electrolytes other than nitrates, acetates, or fluorides could be used in order to determine whether this silver hydrosol is stable toward all electrolytes when so protected by the reversible cellulose colloid. This has not yet been done. The effect of the electrolytes mentioned above refers to silver hydrosols containing approximately one-half per cent silver nitrate. Their effect in the absence of silver nitrate could hardly be different.

However, it has not been possible always to obtain this spontaneous transition of the colloidal to ordinary silver. Very slight variations in the conditions under which the material is prepared or preserved apparently make a great deal of difference in the ease with which it is transformed. This behavior was noticed and investigated by Lea,[29] who states that moisture and light together are favorable to the transition, but that if some specimens are dried and subsequently exposed to light they become very insoluble (i. e., irreversible) and do not undergo transformation to ordinary silver. A very similar behavior has been observed with the red variety precipitated by alcohol. In one instance a specimen of the dark brown variety (from alcohol precipitation) withstood a temperature of 150° C for five hours without losing its characteristic dark brown color by transmitted light, although by reflected light it showed a greenish yellow appearance similar to that of gold. Another sample of the same silver hydrogel treated in the same manner, except that it was not heated, changed to ordinary gray silver on standing under an inverted crystallizing dish in diffuse daylight, the change being observed at the end of eight days. This may have been favored by the presence of moisture as suggested by Lea, but at the time we were not aware of this phase of Lea's investigations and could find no explanation of the difference in the behavior of the two specimens. However, with the very dark brown or black silver sediment which settles spontaneously from silver nitrate solutions that are only slightly contaminated with filter paper, it has been observed that this change from dark brown or blue to yellow and then gradually to ordinary gray or white silver always occurs upon heating for a few minutes at 130° or upon long standing at ordinary temperature.

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[29] Amer. J. Sci., [3] 38, pp. 129 and 237.

In addition to the spontaneous change of the coagulated colloid into ordinary silver, its percentage composition and behavior toward various reagents show conclusively that it is practically pure metallic silver.

(*b*) **Percentage Content of Silver.**—The percentage content of silver was estimated in the following manner: Fifty grams of No. 595 Schleicher and Schüll filter paper was first freed from soluble chlorides and other soluble impurities as far as possible by several extractions with water. These first extracts were discarded to avoid contaminating the silver hydrogel (subsequently to be formed) with silver chloride or other insoluble silver salts. This thoroughly extracted filter paper was then allowed to stand in a covered beaker until practically dry and then again extracted in the usual manner, the extract being filtered first through a sheet of the same filter paper and then through a thick asbestos mat. The hydrosol produced in the usual way was coagulated by the addition of two volumes of alcohol and was collected on asbestos in a weighed Gooch crucible. The gel was washed first with absolute alcohol until the filtrate was free from silver salts and then with a little water; dried at 100° for a few minutes, then over sulphuric acid in a vacuum desiccator and weighed again to determine the mass of residue. The material, after moistening with hot water, was then washed with 30 per cent nitric acid and this treatment repeated until there was no further decrease in weight. In some cases where the precipitate had been subjected to prolonged drying and long exposure to light the dark brown material dissolved very slowly in the strong acid and several treatments with acid were required to produce a constant weight. In one instance concentrated nitric acid was used to hasten the solution, with the surprising result that the residue was transformed from almost black to a brilliant purple color and then dissolved with very great difficulty. Some of this purple material passed through the filter, evidently in colloidal condition, and did not become colorless until after standing several hours in the strongly acid filtrate. This is evidently still another allotropic form of silver which has the very remarkable property of almost complete insolubility in concentrated nitric acid. In no other case was difficulty of this sort encountered, the precipitate being soluble in 30 per cent nitric acid. The silver in the filtrate was estimated with standard ammonium thiocyanate in the usual manner. The results of three analyses of samples varying in weight from 10 to 20 milligrams prepared at different times were:

	Per cent silver
No. 1	97.0
No. 2	96.8
No. 3	96.6
Average	96.8

The remaining 3.2 per cent was probably organic material, since on ignition samples lost approximately this per cent of volatile and oxidizable material.

(*c*) **Behavior toward Various Reagents.**—The following experiments on the behavior of the coagulated colloid, obtained from silver nitrate solutions treated with filter paper extract, were carried out to further strengthen the evidence that this colloid is nearly pure metallic silver.

As already indicated, the behavior of the precipitated silver toward chemical reagents varies somewhat according to the method of preparation. An illustration of this is the purple form, obtained by prolonged drying of the dark red hydrogel precipitated by alcohol, which is practically insoluble in concentrated nitric acid. There are certain properties, however, more or less common to all the forms so far obtained, and these will now be briefly described.

Nitric Acid.—Toward nitric acid all the forms obtained from filter paper extract seem to behave quite differently from those described by Carey Lea. For while they resemble some of his forms in being practically insoluble in very dilute nitric acid, they are not readily converted into ordinary white silver by contact with dilute acids as are his forms. In other words, the presence of dilute acid does not seem to hasten this spontaneous change to ordinary silver which sometimes takes place. The only similar effect is the one mentioned where concentrated nitric acid transformed a dark brown variety to a brilliant purple one.

Ammonia.—The coagulated silver sediments are not dissolved to colorless solutions even by concentrated NH_4OH. This behavior in itself eliminates all the ordinary compounds of silver except silver sulphide, which is excluded by the percentage content of silver and other chemical properties of the material, such as its catalytic action upon hydrogen peroxide. When concentrated ammonia is added to the deep red wine-colored hydrosols, the solution remains practically unchanged except that after the addition of ammonia the hydrosol seems to be more stable, since it is not so readily coagulated by the addition of alcohol. Similar stable colloidal solutions are formed when the coagulated, practically insoluble, sediments are treated on the filter with ammonia water. The precipitate then passes through the filter in colloidal condition. This behavior is similar to that observed by Muthmann with colloidal silver prepared by the reduction of silver citrate by means of hydrogen, except that the ammoniacal hydrosols in the present case are much more stable and are not differently colored from the original hydrosol.

Potassium Cyanide.—All the forms of silver sediment are readily soluble to a clear solution in this reagent.

Hydrogen Peroxide.—A thin film of the red-brown hydrogel (which had been thoroughly washed with absolute alcohol) was spread upon glass and dried in a desiccator over sulphuric acid. When this film, which was slightly yellowish green by reflected light and red brown by transmitted light, was covered with a few drops of a 3 per cent solution of hydrogen peroxide, a copious evolution of gas began immediately. After the action had ceased the film was washed and again dried. The slight green appearance (by reflected light) had entirely disappeared, leaving a homogeneous dark red-brown film.

Here again this striking behavior is entirely similar to that observed by Carey Lea[30] and also by McIntosh[31] with colloidal silver, except that there was very little evidence of a partial solution of the silver, as was observed by the latter, unless the disappearance of the green color may be attributed to the solution of a very thin film of some kind. While it is true that silver oxide acts catalytically upon hydrogen peroxide in a similar manner, the possibility of any appreciable proportion of the sediment consisting of oxide is excluded by its behavior with ammonia, its behavior toward dilute and concentrated nitric acid, and its ready amalgamation with mercury.

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[30] Amer. J. Sci. [3], 38, pp. 129 and 237.

[31] J. Phys. Chem., 6, p. 15 (1902).

Amalgamation with Mercury.—If a little of the dry dark-brown powder obtained from the red hydrosol by precipitating with alcohol be placed in a small porcelain crucible and treated with a globule of mercury, the whole of the powder amalgamates with the mercury at ordinary temperature. The two materials must be brought into intimate contact by stirring with a glass rod. If the silver is in the form of an adherent film upon the glass or porcelain, the amalgamation does not take place, but if the film is scraped loose the action immediately takes place.

(*d*) **Summary.**—It is difficult to explain these properties of the hydrogel obtained from silver nitrate and pure filter paper extract upon any other assumption than that the material is nearly pure metallic silver.

When considered in connection with the other properties described, the evidence is certainly conclusive that filter paper acts chemically upon silver nitrate solution at ordinary temperatures with the production of colloidal metallic silver. The mechanism of the chemical reactions which bring about this result have been examined somewhat in detail and will be discussed later. The manner in which this colloid produces the peculiar striated deposits of silver in the voltameter will be explained on page 279.

G. CHANGE IN THE CONDITION OF NEUTRALITY OF SILVER NITRATE SOLUTIONS PRODUCED BY FILTER PAPER EXTRACT

When silver nitrate is reduced to metallic silver, one equivalent of nitric acid must necessarily be liberated for each equivalent of silver thrown out; consequently, if filter paper extract reduces silver nitrate to colloidal metallic silver, the solution should become acid. The demonstration of this change was considered a very important link in the evidence that the above reaction does actually take place; but when this seemingly simple task was undertaken serious difficulties were encountered. It was soon discovered that the tests could not be made in the presence of the silver nitrate by means of the usual indicators. Litmus solution forms a precipitate with silver nitrate, masking the color reaction and showing that a disturbing chemical change takes place. With litmus paper the results depend upon the manner in which the test is made. If only the end of the paper is dipped into the solution the reaction usually appears to be acid, but this was found to be due to the capillary action of the paper, which results in the acid being drawn up more rapidly than the base (AgOH). A pink band travels up the paper, immediately followed by a blue band. If, on the other hand, the whole strip of paper is immersed at once in the solution, the reaction is invariably basic even after 1 part in 100 000 of free acid is added to solutions prepared from repeatedly recrystallized salt.

With methyl orange, silver nitrate solutions invariably show an acid reaction even after the addition of indefinite amounts of pure sodium or barium hydroxide. So long as any silver nitrate remains the reaction is acid.[32] Since there is no evidence of any reaction between the silver salt and this indicator, and, further, since the intensity of color is uniform for all solutions of the same concentration, this result strongly indicates that silver nitrate is slightly hydrolyzed. When the silver was removed as silver chloride by precipitating with neutral sodium or potassium chloride and filtering, it was found that the filtrate from recrystallized and supposedly neutral silver nitrate usually showed a basic reaction toward methyl orange, litmus, phenolphthalein, and iodeosine. The same results were obtained with solutions strongly contaminated with filter paper, i. e., they usually reacted basic toward all indicators after precipitating the silver as chloride and removing it by filtration. Occasionally a solution which had been standing for many weeks would show an acid reaction, but the freshly contaminated solutions were invariably basic even after considerable of the dark brown sediment had settled from the solutions.

These difficulties were finally explained by the observation that the filter paper extracts themselves show a pronounced basic reaction toward the indicators mentioned.[33] This behavior explained the results just mentioned which were obtained with the recrystallized and supposedly neutral silver nitrate, for the silver chloride was filtered off by means of filter paper, the filtrate extracting more or less basic cellulose from the filter according to how thoroughly it had been washed. Later work showed that recrystallization from neutral solution itself produces a trace of basic silver hydroxide, but this is slight in comparison with the effect of the oxycelluloses. When asbestos filters were employed the recrystallized salt showed a practically neutral reaction after precipitating the silver as chloride. The basic reaction of the freshly contaminated silver nitrate solutions was therefore real, and was due to the filter paper extract itself.[34]

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[32] Richards, Collins, and Heimrod (Proc. Amer. Acad., 35, p. 123) state that the electrolyte near the anode gave an acid reaction with methyl orange, whereas the cathode electrolyte remained neutral toward the same indicator. Later, however (Jour. Amer. Chem. Soc., 29, p. 808), Richards and Forbes state that silver nitrate solution is acid toward methyl orange even after the addition of base. We were not aware of this last observation when the above tests were made.

[33] So far as we are aware this observation is new and should prove of some importance in relation to the chemistry of cellulose. It is no doubt closely related to the electrochemical and absorptive properties of cellulose in general. See Cross and Bevan, Researches on Cellulose, 1900–1905, pp. 7, 103, 128, 131, 157. Also experiment mentioned in this paper on pp. 262–263.

The reduction of silver nitrate (by filter paper extract) results in the production of free acid, which is immediately neutralized by the basic oxycellulose present, the basicity of the solution gradually diminishing until it is entirely neutralized by the acid. As the reduction continues the solution becomes acid,[35] the acidity increasing until a condition of equilibrium is finally reached. This final acidity is often sufficiently high to be detected with litmus paper without previous precipitation and removal of the silver as chloride and may account for the observations of Kahle and others upon the acid reaction of very old repeatedly used solutions, a change which they attributed to the process of electrolysis itself instead of to the reducing action of oxycelluloses from filter paper upon the silver nitrate.

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[34] Ten grams of No. 595 S & S filter paper yield a basic extract (when treated in the manner described) which is equivalent to approximately .47 milligram of sodium hydroxide. The residue left upon evaporation of such an extract at a temperature of 100° C is approximately 17 milligrams. If it be assumed that this is a single definite oxycellulose and not a mixture, we have the result that the equivalent weight of oxycellulose is approximately 1447 (in terms of hydrogen). These figures are to be considered only very rough approximations, but they illustrate what we believe to be a new means of estimating the equivalent magnitude of one of the modified forms of cellulose (oxycellulose). The fact, however, that this material is colloidal may vitiate this method of determining the molecular weight of the substance, since its basic reaction may be an absorption phenomenon rather than a true reaction of hydroxyl ions. The colloidal phase of the chemistry of cellulose has recently been emphasized by Cross and Bevan. (Researches on Cellulose, 1900–1905, Longmans & Co., 1906, pp. 6, 126, and 177.)

[35] The neutral nitrate salts or esters of these basic compounds are evidently as strongly reducing in character as the free bases themselves.

TABLE II

Formation of Acid by Action of Filter Paper Extract on 10 per cent Silver Nitrate Solution

Solution tested	Time	Reaction toward iodeosine.	Amount of free acid in parts per million of HNO_3	Amount of free base (in parts per million of equivalent amount of HNO_3
Original aqueous filter paper extract.	Immediately after preparation	Basic		24
Contaminated solution	After 2 hours	do		12
Blank solution	do	do		3.6
Contaminated solution	After 2 days	do		0.6
Blank solution	do	do		2.4
Contaminated solution	After 11 days	Acid	1.8	
Blank solution	do	Basic		2.4
Contaminated solution	After 60 days	Acid	10.8	
Blank solution	do	Basic		2.2
Contaminated solution	After 177 days	Acid	10.2	
Blank solution	do	Basic		3.0

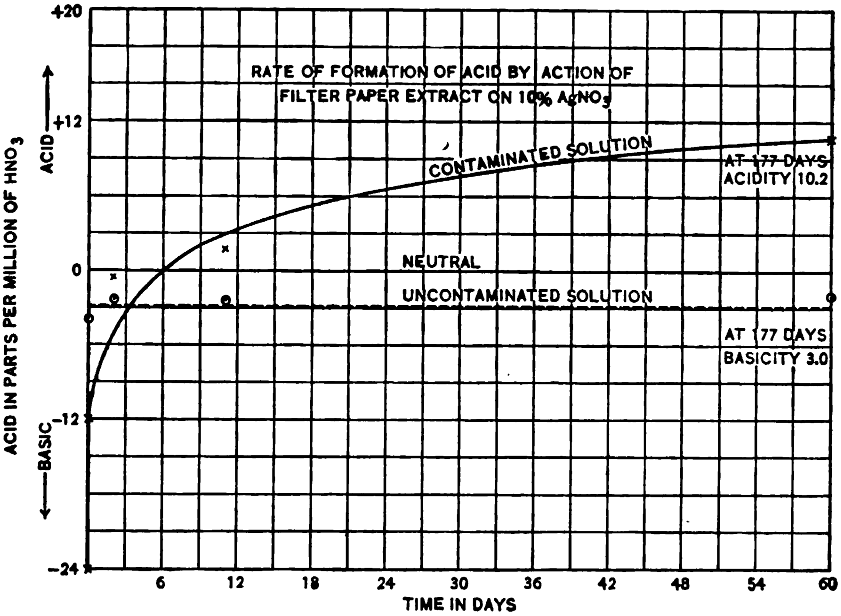

Fig. 26.—*Curve showing the rate of formation of acid by the action of filter paper extract on 10 per cent* $AgNO_3$

Many observations have been made upon electrolytes strongly contaminated with filter paper, and it has been uniformly observed that they are always basic immediately after preparation, the basicity gradually decreasing with time until neutral and then gradually increasing in acidity. The accompanying table (II) and curve (Fig. 26), prepared from the data given, is a single illustration of the course of this reaction. It will be seen that an uncontaminated solution was subjected to the same treatment and tested in the same manner as a control experiment. The contaminated solution was prepared by adding 10 per cent of pure neutral silver nitrate crystals to 50 cc of a filter paper extract made by several extractions of 12.5 grams of No. 595 S & S filter paper. This extract was approximately 24 parts per million basic. Two hours after adding the silver nitrate the basicity had decreased to only 12 parts per million, thus showing that a corresponding amount of reduction had taken place (equivalent to approximately 20 parts per million of colloidal metallic silver) during the time required to make a voltameter determination. No test was then made until after two days, when the solution was found to be practically neutral, but this condition was probably reached much sooner, so that the curve is probably not sufficiently steep in this portion to represent the true change. After becoming neutral or slightly acid the change progresses more slowly.

It should be stated also that the red color of the silver hydrosol begins to develop in such strongly contaminated solutions after a very few minutes at the usual temperature of the electrolyte in the voltameter, i. e., 25° to 30°. This is further evidence that colloidal silver is actually formed in the filter paper voltameter during the time required for a determination. Of course with slightly contaminated electrolytes this color change is not visible.

H. CELLULOSE AS A STRONG REDUCING AGENT

1. GENERAL STATEMENT

The remarkable similarity in the effects of filter paper on the one hand and of very strong reducing agents on the other upon the appearance of the electro-deposited silver had furnished striking evidence that the activity of the cellulose must be due to its action as a very strong reducing agent. This action of cellulose was in strong contrast to that of such mild reducing agents as cane sugar and starch, which were found to be inactive in the voltameter. This indirect evidence of the strongly reducing character of filter paper extracts had been fully confirmed by the experiments just described, in which permanent colloidal solutions of metallic silver were prepared from filter paper and silver nitrate and the metallic silver coagulated and identified by its properties. Moreover, these colloidal silver solutions were prepared under exactly the same conditions which obtain in the voltameter itself. The relative inactivity of cane sugar under the same conditions is further discussed in the next paragraph.

2. RELATIVE RATES OF REDUCTION OF SILVER NITRATE BY CELLULOSE AND BY CANE SUGAR

A better appreciation of the strength of the reducing action of cellulose is obtained when one considers the rate at which acid is produced by the reducing action of filter paper extract as compared with that of cane sugar. Even when relatively very large quantities of cane sugar are added to silver nitrate solution the neutrality remains practically unchanged for several days, as shown by the iodeosine test described in a later section. Less than one part of nitric acid in a million is formed after two days, whereas in the case of filter paper extract more than 12 parts per million of nitric acid is formed in 2 hours, as is shown in table II. In other words, the rate of reduction by filter paper extract is at least three hundred times greater under the same conditions than the rate of reduction by cane sugar.

3. CELLULOSE NOT READILY DECOMPOSED INTO REDUCING CARBOHYDRATES

The question at once arises: How does cellulose function as a stronger reducing agent (under the conditions named) than other carbohydrates of lower molecular weight, such as cane sugar? It seemed probable, notwithstanding the generally greater reactivity of the simpler carbohydrates, that in the present instance the cellulose might be thus easily hydrolyzed, to a very slight extent at least, into reducing carbohydrates of some kind. The concentrated filter paper extracts were therefore carefully examined for such "reducing sugars" by the usual methods, viz, by means of Fehling's solution and also with the polariscope, but with negative results. Owing to the well-known difficulty of standardizing the Fehling test, the method used in the present case is described somewhat in detail.

It had been observed that the aqueous extract of a given weight of filter paper prepared by repeated extraction with the same portion of water is even more efficient in producing striæ than the filter paper itself; consequently it seemed probable that the reducing carbohydrates could be concentrated in this manner. It was therefore thought best to test such aqueous extracts for "reducing sugars" rather than to apply the test directly to the cellulose fiber, especially since the separation of the cuprous oxide would in the latter case not be complicated by the presence of the cellulose fibers. Moreover, solubility in water is a characteristic property of the "active" material (or of the material from which it is formed), so that the test upon aqueous extracts would have a correspondingly greater significance.

In preparing these extracts 50 grams of the filter paper was cut into small pieces about a centimeter square, placed in a beaker, covered with 300 cc of distilled water, and kept at 35° for from 10 minutes to several hours. The water was either drained off in the centrifuge or squeezed out with thoroughly cleansed hands and the extract filtered through a sheet of the same kind of filter paper. Usually this treatment was repeated several times with the same portion of water in order to concentrate the "active" substance, and in some instances large volumes of the extract so prepared were evaporated nearly to dryness for the same reason. These extracts were rendered very faintly acid by the addition of from 1 to 10 parts of nitric acid to each 100 000 parts of extract and allowed to stand for varying lengths of time before being tested for reducing carbohydrates. The amount of nitric acid added was intended to be slightly in excess of the quantity likely to be present (due to hydrolysis) in 10 per cent solutions of silver nitrate.

With the filter paper extracts prepared as described above and acidified by the addition of a few parts in a hundred thousand of nitric acid, we were unable to obtain any test for reducing sugars either by means of the polariscope or with Ost's modification of the Fehling test.[34] In several instances the acidified extracts were allowed to stand several days at ordinary temperature before being tested in order to allow ample time for any hydrolytic action which might take place (under conditions of temperature and concentration of acid comparable to those which obtain in the filter paper voltameter) to complete itself; but the results of these tests were the same as for the recently acidified extracts. Extracts prepared by digesting the filter paper with 10 per cent solution of silver nitrate likewise gave no test for reducing sugars. Several trials showed that a few parts in one hundred thousand of dextrose, if added either to the plain aqueous extracts or to extracts containing silver nitrate, could readily be detected by means of Ost's test. The polariscope method was less sensitive, but filter paper extracts to which a part in ten thousand of dextrose had been added showed a very small but appreciable rotation in the polariscope. (The column of solution examined was 20 cm in length and the rotation corresponded to approximately 0.03 per cent of cane sugar on a scale calibrated directly in percentages of cane sugar.)

It is certain, therefore, that if dextrose or any similar sugar is formed in the filter paper voltameter it can not be present in amounts greater than 1 part in 100 000. The limit is probably very much lower than this, since the tests were made on much more concentrated extracts than are normally present in the filter paper voltameter.

4. MECHANISM OF THE REDUCING ACTION OF CELLULOSE EXTRACTS—DECOMPOSITION INTO FURFURALDEHYDE

The fact that these filter paper extracts do not exert an appreciable reducing action upon Fehling's solution and are not optically active, is in strong contrast with their very vigorous reducing action upon neutral or slightly acid silver nitrate solution and further emphasizes the radical difference in the behavior of these "soluble" celluloses on the one hand and of the simpler carbohydrates such as cane sugar and starch upon the other, especially toward silver nitrate solution. Furthermore, this behavior strongly indicates that the decomposition of these "soluble" celluloses takes place in an entirely different manner from that of a resolution by hydrolysis into hydrocelluloses or reducing carbohydrates having free CO groups, as is the case with cane sugar and starch.

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[34] Of the numerous modifications of the Fehling test, best results were obtained with Ost's modification (Chemiker-Zeitung, **19**, pp. 1784, 1829 and 1830), using a solution containing only 1 gram of $CuSO_4 + 5H_2O$ per liter. The great advantage of this test lies in the greater certainty with which the blank determinations may be controlled, since no weighable precipitate is formed upon boiling the solution for ten minutes, even after diluting it with half its volume of water.

In carrying out the test for reducing sugars with this reagent 50 cc of the extract and 100 cc of the copper solution in an Erlenmeyer flask of 500 cc capacity was quickly heated and maintained at the boiling temperature for 10 minutes. The solution was then quickly cooled under the tap, filtered through an asbestos Gooch, in the usual manner, the precipitate washed successively with measured volumes of 10 per cent potassium bicarbonate solution, hot water, alcohol, and ether, dried at 110°C, allowed to cool, and then weighed. The weight of cuprous oxide was checked by washing the filter with dilute nitric acid, then with water, drying and weighing again. In some instances, as a further check upon the blank tests, the nitric acid filtrate was tested for copper with ammonia. It was found possible by means of this test to detect 0.001 per cent of dextrose in solution in distilled water.

The conclusion was finally reached that the reducing action upon silver nitrate solution takes place through the intermediate formation of furfuraldehyde (or some of its homologues). This could result either from the decomposition of pure cellulose hydrates or possibly from the closely related pentosans which might be so intimately associated or combined with the cellulose that they could not be further separated from pure cellulose by any of the means which we had employed for extracting the soluble impurities from filter paper.

Furfuraldehyde, when present in solution to the extent of 0.1 per cent or less, does not reduce Ost's modification of Fehling's solution (with 10 minutes' boiling) to any appreciable extent, and hence might not have been detected in the tests made with this reagent. With ordinary Fehling's solution it can be more readily detected, but even with this reagent it is necessary to boil the solution for a much longer time (a half hour) to insure complete oxidation of the aldehyde.[37] Being optically inactive it could not be detected by means of the polariscope test. It seemed perfectly possible therefore that furfural might have been present in the extracts which were tested for "reducing sugars" and yet have escaped detection by the tests used.

We were aware that this aldehyde is generally regarded as a product of the condensing action of strong acids upon pentoses only. Since pure cotton cellulose ($C_6H_{10}O_5$) is a hexopolyose, one would not expect it to yield furfuraldehyde. Indeed, as is well known, the yield of furfuraldehyde is taken as the indirect measure of the amounts of certain "modified" or "noncellulose" constituents present as "impurities" more or less intimately mixed or combined with the pure cotton cellulose.

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[37] This difficulty with ordinary Fehling's solution may be due to the resinifying action of the strong alkali upon furfural, which is much more sensitive to this effect of alkalis than dextrose.

Examination of the more recent literature pertaining to this phase of the chemistry of cellulose disclosed the fact, however, that all classes of celluloses, hexopolyoses as well as pentopolyoses (or pentosans), yield furfural, but in greatly varying amounts, on treatment with strong condensing agents. For example, Suringar and Tollens (Zs. angew. Chem., 1897) found that raw cotton, while containing no pentosans, yet yielded very slight traces of furfural as one of the products of acid hydrolysis. Therefore it seemed well worth while to test various filter paper extracts to determine whether this strongly reducing aldehyde is formed under conditions comparable to those which obtain in the voltameter.

5. TESTS FOR FURFURALDEHYDE

The test employed for furfural was that described by Förster (Ber., **15**, 320), in which two-thirds of the liquid to be tested is distilled off, the distillate extracted three times with chloroform, the combined extracts evaporated nearly to dryness, taken up with a little alcohol, and tested with an equal volume of a mixture of equal parts of glacial acetic acid and redistilled, colorless xylidine. If furfural is present, a red color develops. The first tests for furfural in acidified filter paper extracts were made in November, 1909. About 20 grams of Schleicher and Schüll filter paper (No. 595) was extracted with 300 cc distilled water in the manner described on page 253. This was acidified by the addition of approximately 0.01 per cent of nitric acid and allowed to stand overnight before distilling. The amount of nitric acid added was intended to be no greater than that probably present in pure silver nitrate solutions due to slight hydrolysis. When tested in the way described above, these distillates showed very distinctly the presence of furfural. In later experiments an attempt was made to form an estimate of the amounts of furfural which could be obtained under these exceedingly mild conditions from definite weights of filter paper and also the effect of various treatments of filter paper upon the yield. These tests were carried out according to the method adopted by the Association of Official Agricultural Chemists for the estimation of furfural in distilled liquors (Bull. No. 107, U. S. Department of Agriculture, p. 96).

In each of these tests 50 grams of the filter paper to be tested was digested with 350 cc of water for 30 minutes at a temperature of 35°. The extract was acidified by the addition of approximately 0.01 per cent of nitric acid, and after being allowed to stand for varying lengths of time 200 cc was distilled off. Of this distillate, 50 cc was tested directly with 2 cc of colorless xylidine and 0.5 cc of hydrochloric acid (sp. gr. 1.12) and kept for 15 minutes in a water bath at about 15° C. The estimation was made by comparing the intensity of the color developed with that obtained from standard solutions of furfural of known strength tested in the same manner. The solutions and reagents were always cooled to the same temperature before mixing, and blank tests with distilled water were carried out as checks upon the purity of the reagents used. The color develops in from 5 to 15 minutes, after which it may fade or the blank may show a brownish red color. It was found to be advantageous to make the test (as described) without the use of alcohol, which had a tendency to give a yellow color which partially masked the red. In fact, in several instances tests which showed bright red color without the alcohol turned yellow upon the addition of alcohol. This was probably due to the more complete solution by the alcohol of coloring matter (oxycelluloses?) present.

The results obtained with different samples of filter paper after having been subjected to various treatments intended to remove impurities are tabulated in Table III, following.

TABLE III

Showing Yield of Furfuraldehyde from Filter Paper

Previous treatment of filter paper	Solvent	Treatment of acidified extract		Yield of furfuraldehyde
		Time	Temperature	
		Hours	° C	(Mg)
None	Water	2	70	2
Do	do	12	35	Trace
Extracted with water and immediately tested	do	12	70	None
None	1% KOH	2	35	20
Extracted with 1% KOH, then with water, and immediately tested	do	2	35	Trace
Do	Water	2	70	None
Extracted with water and allowed to dry one week	do	2	70	5
Do	do	24	35	Trace

The yield of furfural is expressed in milligrams obtained from 50 grams of dry filter paper when treated in the manner described.

These experiments show conclusively that furfuraldehyde is formed by the action of nitric acid of a concentration comparable to that probably present in 15 per cent silver nitrate solution due to hydrolysis. Treatment with concentrated hydrochloric acid as in the standard methods used in estimating the furfural constituents of cellulose would undoubtedly yield much larger amounts. But this of course was not the object of the present tests.

The amounts of furfural obtained by the methods in the foregoing tests are of course not to be considered as an accurate measure of the total quantities which can be formed by the action of silver nitrate in the voltameter, for the conditions, while as nearly alike as it was possible to make them, are yet dissimilar in some important respects. Under actual conditions the furfural may be removed from the field of action as rapidly as it is formed by interaction with silver nitrate. Thus the condition of equilibrium existing between the soluble cellulose product and furfural would continually be disturbed so that more furfural would be formed. The amounts obtained from acidified aqueous extracts would therefore probably be far less than the amounts formed by the action of silver nitrate under the same conditions.

When furfural reduces silver nitrate, it is itself of course oxidized to pyromucic acid.[38] The presence of pyromucic acid (or its derivatives) in silver nitrate solutions which have been partially reduced to metallic silver by filter paper extracts would constitute, therefore, the most direct evidence possible to obtain that the reduction had been brought about primarily by the decomposition of the filter paper into furfuraldehyde. We have made a few preliminary qualitative tests for this acid, but those so far employed do not appear to be sensitive enough for the present case, so that a complete isolation of the acid seems to be necessary.[39]

In this connection the decomposition products of furfural itself when treated with silver nitrate should be examined.

I. EFFECTS OF FURFURALDEHYDE IN THE VOLTAMETER

When testing the effects produced by the addition of strong reducing agents to the electrolyte we had observed that, of all the aldehydes tried, furfural seemed to be the most efficient in imparting a striated appearance to the electro-deposited silver. (Fig. 25). These results were obtained with Kahlbaum's c p furfural from freshly opened, hermetically sealed, glass bulbs. With redistilled furfural the effects were not so pronounced. Repeated tests showed that the dark colored polymerized furfural was most effective in reproducing the effects caused by filter paper. In one experiment a sample contained in a sealed glass bulb was heated in water contained in a glass beaker for several days while exposed to strong sunlight until it had become quite dark and viscous. An electrolyte containing one one-thousandth of 1 per cent of this polymerized furfural when electrolyzed gave a strongly striated deposit similar in all respects to that obtained in the filter paper voltameter. In fact the deposit could not be distinguished from that obtained from a Rayleigh voltameter. Under the microscope the deposit had the noncrystalline "lava like" appearance so characteristic of deposits obtained from electrolytes strongly contaminated with filter paper. Just why this polymerized furfural should give more pronounced effects than the redistilled liquid was not quite clear. However, it did not seem improbable that the furfural formed from filter paper (assuming this actually occurred) would be in a similar physical state (i. e., polymerized or condensed) when first formed. In this connection it may be well to mention the fact that a very dilute solution of polymerized or "metafurfural" has a light yellow color exactly similar to that of concentrated filter paper extracts. However, we do not wish to place emphasis upon this circumstance, but it undoubtedly indicates a close relationship of both furfural and the filter paper extract to the oxycelluloses. This subject will be referred to again in the next section.

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[38] One of the standard methods for preparing pyromucic acid is to oxidize furfural with moist silver oxide.

[39] We hope to be able to return to this phase of the question in the near future, not only because of its bearing upon the voltameter problem, but more especially because of its relation to the chemistry of cellulose.

J. SPONTANEOUS DECOMPOSITION OF CELLULOSE INTO OXYCELLULOSE AND THE RELATION OF OXYCELLULOSE TO FURFURALDEHYDE

The effects of the various treatments of the filter paper upon the yield of furfural obtained from the aqueous extracts indicate that the soluble substances which yield furfural can be removed from the filter paper by extracting with water or more effectively with caustic alkali. These soluble furfural-yielding substances are formed again, however, if the filter paper is allowed to stand for some time before a second extraction. In the experiment described on page 231, the filter paper was subjected to repeated treatments with water to completely extract the "active substance" (which we then thought must be present as an impurity), but it was found that this treatment apparently had no effect upon the activity of the filter paper in the voltameter. This result was no doubt due to the fact that the extracted filter paper had been allowed to stand several days to dry before again testing its effect in the voltameter.

This behavior of thoroughly extracted filter paper on standing exposed to ordinary conditions has been observed a great many times. If the extracted paper has stood four or five months the extract then is even more strongly colored (yellow) than the original extract and possesses all the other properties of the first extract to the same or even greater degree; it reduces silver nitrate to colloidal silver quite as readily, yields furfural when distilled with very dilute nitric acid, and shows the basic reaction with iodeosine and methyl orange. If after the first thorough extraction the moist pulp is again extracted within two or three days, the washings are then not so strongly colored as in the first case, but are even more basic and quite as strongly reducing toward silver nitrate. In one case the second extract (made two months after the first treatment) was 7 parts per million basic, whereas the first extract made in the same manner was only 1.8 parts per million basic. The relation between these properties and the amounts of soluble solids extracted under varying treatments is an interesting field which we hope to investigate further at some future time.

The foregoing observations indicate that the soluble furfural-yielding substances are formed by a spontaneous decomposition of the cellulose, due perhaps to slow oxidation in the air or to fermentation or to both causes combined, the final result being the formation of oxycelluloses, as is shown both by the readiness with which the extracted material yields furfural when distilled with dilute acid and also by the yellow color of the aqueous extracts and especially of the alkaline extracts.

The spontaneous decomposition takes place only to a limited extent and seems to be confined mostly to the surface of the fibers.

Undoubtedly the physical structure of cotton cellulose, offering as it does an enormous surface for the action of atmospheric oxygen, explains in part at least this tendency of filter paper to become superficially oxidized. In this connection, it should be mentioned that Förster has observed the similar decomposition of cane sugar into furfural by the action of very dilute acids, and it seems entirely probable that in this case also the decomposition into furfural is rendered possible by a previous slight oxidation of the sugar—a process which probably takes place much more slowly and to a less extent than in the case of cotton cellulose, owing to the difference in surface conditions; hence the greater activity of cellulose in the voltameter. This spontaneous decomposition of cellulose probably accounts also for the results of Suringer and Tollens in obtaining furfural from pure hexopolyoses.[40]

Before leaving this phase of the problem it is desired to again emphasize the striking similarities between solutions of polymerized or condensed furfural and concentrated filter paper extracts (oxycellulose), especially as regards their action in the voltameter. These effects were so similar that this fact alone was at the time considered sufficient evidence that the effects of filter paper were due entirely to furfural. In addition it should be stated that when silver nitrate is added to such furfural solutions colloidal silver hydrosols are obtained which are exactly similar in color and other properties to those prepared with filter paper extract. When these facts are considered in connection with the fact that furfural is so readily formed from these filter paper extracts, the similarities between these two substances certainly appear to be more than a coincidence and indicate a very close relationship in their chemical constitution. The one important dissimilarity is their reaction toward indicators—oxycellulose showing a well-marked basic reaction toward both methylorange and iodeosine, whereas polymerized furfural is neutral or faintly acid toward the same indicators. However, it should be stated in this connection that upon electrolysis we have recently found that oxycellulose is decomposed into equivalent amounts of an acid

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[40] Many well-known facts are in accord with the foregoing views, that the decomposition of pure cotton cellulose into furfuraldehyde takes place through the intermediate formation of oxycellulose. A few of these facts may be mentioned at this point: (1) The yield of furfural is used as an approximate measure of the oxygen in oxycelluloses in excess of that indicated by the formula $C_6H_{10}O_5$ as determined by elementary analysis. (2) All carbohydrates, including hexoses and polyoses derived from them, yield large amounts of furfural when treated with concentrated sulphuric acid, which is a strong oxidizing as well as a strong hydrolytic agent. This decomposition is not brought about by nonoxidizing acids, e. g., HCl. (3) Hexoses can be oxidized first to the corresponding acid, then by means of H_2O_2 to a pentose which decomposes directly into furfural by the condensing action of HCl, the reactions involved being expressed by the following equations:

$$\underset{\text{hexose}}{CH_2OH(CHOH)_4CHO} + O = \underset{\text{corresponding acid}}{CH_2OH(CHOH)_4COOH}$$

$$CH_2OH(CHOH)_4COOH + O = \underset{\text{pentose}}{CH_2OH(CHOH)_3CHO} + CO_2 + H_2O$$

(4) Levulose (a keto-hexose) is converted directly into a derivative of furfural by treatment with anhydrous hydrobromic acid, which is both a very strong condensing acid and a strong oxidizing agent.

In general, the conversion of either a simple hexose or a hexopolyose, such as cotton cellulose or cane sugar, into furfural or its derivatives by the condensing action of acids seems to be conditioned by a previous oxidation of the carbohydrate. The mechanism of this decomposition may be as indicated in (3) above. However, it is not necessary to assume that a pentose is actually formed, for the three processes—hydrolysis to hexose, oxidation to pentose (accompanied by elimination of water), and finally the condensation of the pentose to furfural—may be in the end equivalent to oxidation and condensation, so that complete hydrolysis need not take place.

variety and a basic variety, both of which retain their colloidal character and reducing power toward silver nitrate.

III. STRIATIONS AND THEIR EXPLANATION

A. INTRODUCTION

During the interval between September 22 and December 17, 1909, a large number of qualitative experiments were conducted, and the chemistry of the silver voltameter further studied. Among other things, we studied the question as to what causes the striæ in a filter paper voltameter, or in a deposit which is made from a solution that has been contaminated by filter paper extract, or by linen, cotton, wood fiber, or certain other substances. Striæ have been observed in silver voltameter deposits by a great many observers, ever since the experiments of Kirmis published in 1876. Few observers have ever hazarded an opinion as to their cause, and no one has given a satisfactory explanation of their production. We have confirmed the observations of Smith that the presence of striæ is evidence of an impure electrolyte, which is quite contrary to the opinions of earlier observers, who believed striæ were always present.

Before describing our own experiments, however, we shall describe briefly some of the previous work on the subject.

B. EARLY WORK

1. KIRMIS

In 1876 Kirmis undertook some experiments on the migration of the ions at the University of Berlin upon the suggestion of Helmholtz, in which he employed a silver voltameter to measure the quantity of electricity passing through his apparatus. His attention was drawn to the various forms in which silver is deposited out of a silver nitrate solution, and he described some of these forms in a separate paper.[41] Well-marked striæ appeared on the bottom of the cylindrical vessel radiating from a center immediately under the pointed anode, and these lines extended up the sides of the vessel as parallel lines at a constant distance from one another. He made a large number of experiments, varying the strength of current, duration of the deposit, concentration of the electrolyte, and total electromotive force in the circuit. He found the best results with 5 to 10 per cent solutions of $AgNO_3$, current not greater than sufficient to deposit 0.28 mg of silver per minute per sq. cm, and a sharp-pointed anode. He also thought a high voltage an advantage, even if the current were unchanged. He does not offer any explanation of the cause of striations, but says that the assumption that they are caused by currents in the electrolyte is not very probable, the regularity of spacing seeming to offer a serious difficulty to this view.

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[41] Pogg. Ann., 158, p. 121, 1876.

2. BEHN

In 1894 Behn published an elaborate paper [43] on the subject of striated deposits in the silver voltameter. This work was done under the direction of Kundt and, like that of Kirmis, was carried out at the University of Berlin. He studied very carefully the conditions under which striations occur, and sought for an explanation of the cause of striations. He first used a platinum crucible as a cathode and a vertical rod (pointed at the bottom) as an anode. No filter paper or other substance surrounded the anode, and no glass or other dish was placed under it. A 25 per cent solution of silver nitrate was used as electrolyte. With a single accumulator as a source of current he passed 0.1 ampere for one hour through the voltameter, and obtained a well-marked striation of the deposit, as Kirmis had obtained. He therefore concluded that a high electromotive force was unnecessary if the resistance of the circuit was not large.

In order to photograph the deposits easily he replaced the platinum crucible by a cylindrical glass cup lined with sheet platinum, a disk of platinum covering the bottom and a long strip of platinum bent into a circle forming a lining to the walls of the cup. After a deposit was made using the sheet platinum as a cathode the latter was removed from the cup and laid out flat and photographed. Numerous pictures of deposits are given by Behn, which agree in appearance with some of the deposits made by ourselves. Behn found (confirming Kirmis) that the striæ radiate from the point at the bottom of the cup under the anode, and are vertical on the sides of the cup. That the direction of these striæ was determined by the convection currents circulating in the electrolyte, he showed by numerous ingenious experiments. First of all, he made a special voltameter cell with parallel walls of glass, a section of which is shown in Fig. 27, which permitted seeing the convection currents while the electric current was flowing and the striated deposit was forming. The cathode was a strip of sheet platinum bent into a semicircle. As soon as the current begins the electrolyte around the anode begins to increase in density, whereas the electrolyte on the surface of the cathode decreases in density. Hence convection currents are set up, as shown in the figure, which are the more rapid as the current is stronger. The direction of these currents is precisely the same as the direction of the resulting striæ. This was found to be true when the cell was closed at the top and turned on its side; the striæ changed in position to correspond with the new course of the convection currents. When, however, the cathode was horizontal and at the top of the cell and the anode at the bottom, so that the heavy anode liquid remained at the bottom and the impoverished cathode liquid collected at the top, there were no appreciable convection currents and *no striæ appeared* in the deposited silver. It was therefore clear that the direction of the striæ was determined by the direction of the convection currents, and that striæ could not occur in the absence of convection currents. Why this was so and what was the primary cause of striations was a question Behn studied carefully, but could not answer satisfactorily to himself. He did, however, venture a suggestion. He says: "But how the striæ arise is by far harder to answer. Apparently the flow in the liquid hinders the deposit of silver crystals. At first, the latter deposit themselves on the smooth surface in a completely irregular manner. Through these hindrances the current of liquid upon the cathode is split up into separate filaments and now the deposit takes place almost exclusively between each pair of such filaments. However, this is only an attempt at an explanation."

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[43] Wied. Ann., **51**, p. 105, 1894.

Behn "attempted to learn by the aid of a microscope the manner in which the silver crystals which deposit out at first irregularly arrange themselves in striæ. This did not, however, succeed.

It is probable that the crystals thrown down later deposit themselves in the shelter of those deposited earlier, that is, behind the first with respect to the direction of flow." This is of course no explanation of the phenomenon.

Behn also investigated the effect of varying the concentration of the electrolyte and the density of the electric current. He found the striæ more distinct and farther apart in the more concentrated solutions, and more distinct with smaller current density at the cathode than with larger. With increasing temperature the striations become more distinct, and with purer solutions less distinct. He was surprised at the change in the striæ due to very small impurities in the electrolyte, but apparently did not obtain deposits entirely free from striations.

3. SMITH, MATHER, AND LOWRY

Smith, Mather, and Lowry[43] in their work published in 1908 gave considerable attention to the subject of striations. They observed, as others have done before them, that with pure electrolyte striæ do not appear in the Richards form of voltameter. Also with pure $AgNO_3$ in the Rayleigh voltameter as they employed it the striæ were faint or absent. They regarded striæ as evidence of an impure electrolyte, and attempted to explain the greater tendency for striæ to appear in the Rayleigh voltameter than in the Richards type, by a difference in the convection currents. They varied the concentration and the density of the electric current at the cathode and confirmed Behn's observations as to the marked differences in the striation produced thereby. After giving a careful description of the convection currents arising from the differences of pressure due to the heavy anode liquid in the center of the voltameter and the lighter cathode liquid adjacent to the outer walls of the platinum dish, they give the following statement of their interpretation of the observed effects:

> We interpret these results in the following manner: The film of liquid in contact with the cathode has a greater mean thickness in the 1½ per cent solution than in the 15 per cent solution. This follows because the rate of deposition of silver is the same in each voltameter. If the film is very thin, it is unstable and breaks up into cylindrical columns of liquid. Hence, in contact with the cathode surface there are columns of liquid of low concentration, and in between these the electrolyte is of approximately normal concentration. The latter has the higher conductivity, and since in addition

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[43] Phil. Trans. 207, p. 545.

there is an E. M. F. acting from the columns of low concentration toward the main body of the electrolyte, the current will pass into the cathode through the liquid in between the columns. Immediately the concentration falls and possibly the resultant liquid of small density is pulled into the columns of low concentration. If our assumptions are correct, an increase in the current should result in the cathode film becoming thicker and more stable, and when it is sufficiently stable to remain as a film a striated deposit should not be formed. This was tested by experiment and found to be so.

The following table indicates the results. All the solutions were pure, and the same volume of electrolyte (350 cc) was taken in each case.

Experiment	Electrolyte	Current	Character of deposit
	Per cent	Amperes	
1	1.5	0.1	No striæ
2	3.0	0.7	Do.
3	2.0	1.0	Do.
4	15.0	0.1	Marked striæ
5	15.0	0.3	Do.
6	15.0	0.7	Striæ, but not so marked as in (4)
7	15.0	1.0	Very faint striæ at bend of bowl
8	15.0	2.0	No striæ
9	15.0	4.0	Do.
10	15.0	8.0	No striæ; fine matte surface
11	50	1.0	Striæ

It appears that for solutions of all concentrations striated deposits are obtained for small current densities at the cathode, and matte deposits for very large current densities.

We may now compare the changes in the Rayleigh and Richards forms of voltameter. In the latter case there is no descending anode liquid, and there will be, therefore, less tendency for a star-like deposit to be formed on the base of the bowl. In our own form of Richards voltameter the volume of cathode liquid was in general about 250 cc, and during electrolysis the mean concentration of the solution must have diminished from 15 to 10.6 per cent. The mean concentration of the electrolyte in the Rayleigh form remains constant and, in consequence, for the same current density striæ were produced in the Rayleigh form when they were absent in the Richards form. This effect has also been observed by Guthe[44] and by van Dijk.[45] In the Richards form, as employed by the latter observer, the cathode liquid consisted of about 30 cc of a 20 per cent solution, and at times nearly 3 grams of silver were deposited, the concentration being thus reduced to about 4.3 per cent. Professor van Dijk observed little or no striæ in the Richards form, but marked striæ in the Rayleigh form.

It will be observed that the explanation of Smith, Mather, and Lowry is similar to that of Behn in supposing that the electrolyte next to the cathode surface is split up into columns or filaments.

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[44] Phys. Rev., 19, p. 147; 1904.

[45] Ann. der Phys., 19, p. 271; 1906.

Behn supposes this to be due to the crystals themselves, and that the silver deposits out after this condition is established chiefly between the filaments, thus causing the more or less distinct ridges of silver which constitute striæ.

Smith, Mather, and Lowry, however, suppose that if the film of low concentration in contact with the cathode is very thin, as when the body of the electrolyte is of relatively high concentration, "it is unstable, and breaks up into cylindrical columns of liquid," and that these columns of low concentration are interspersed regularly with columns of high concentration and that the current enters the cathode through the latter.[46] This gives rise to the ridges of silver constituting the striæ, the spacing between which give a measure of the width of the columns.

This explanation is unsatisfactory for several reasons:

1. The existence of separate columns of liquid of different concentrations, or of the same concentration (Behn), is an assumption for which there is no satisfactory evidence.

2. The striæ disappear completely when the electrolyte is pure, and the existence of the columns of electrolyte assumed by Behn and Smith, Mather, and Lowry is in no way dependent upon the slight impurities which are essential to striations.

3. It is impossible to conceive columns of liquids of so small lateral dimensions as the distance between striæ maintaining themselves intact, with other columns between them of greatly different concentration; especially since the silver is supposed to deposit out of the columns of high concentration, which "immediately" reduces the concentration. How these depleted columns could have their concentration suddenly restored in order to keep up the process is impossible to imagine.

4. The lack of striæ in the Richards voltameter is not due to the hindrance which the porous cup offers to the convection currents, as Smith, Mather, and Lowry suppose. For if the porous cup be removed and no filter paper or any septum employed in its place the striæ are still absent, supposing pure electrolyte to be employed. We have demonstrated this repeatedly, and give in Fig. 28 a picture of such a deposit.

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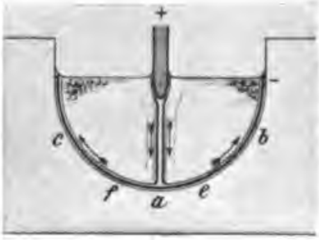
[46] See paragraph quoted above, p. 267.



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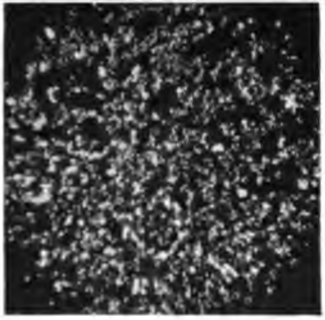

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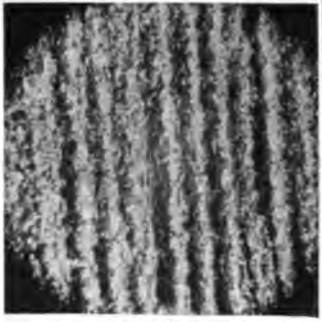

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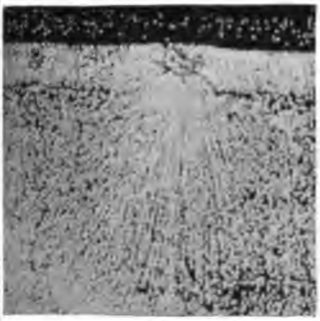

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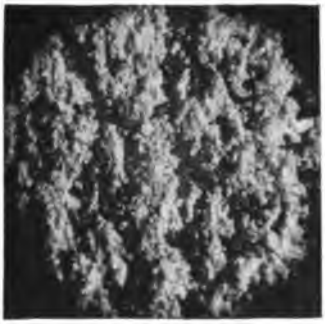

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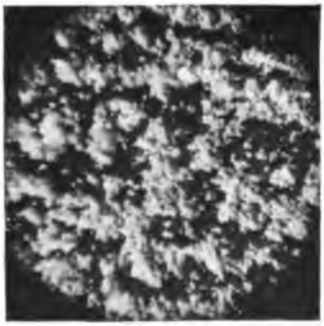

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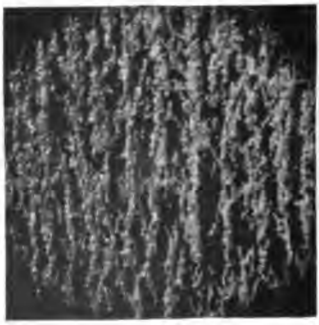

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Fig. 27.—*Behn's special cell with semicircular cathode and parallel glass walls*

Fig. 28.—*Unstriated deposit made in voltameter without septum*

Fig. 29.—*Parallel vertical striae on side of dish.* × 8

Fig. 30.—*Striations radiating from point of discharge of a contaminated electrolyte*

Fig. 31.—*Spiral striae due to rotating the cathode in a contaminated electrolyte, natural size*

Fig. 32.—*Striae growing horizontally from edge of stationary cathode, due to rotation of the electrolyte around it.* × 8

Fig. 33.—*Noncrystalline, slightly striated deposit on under side of cathode inclined 25° to the horizontal.* × 16

Fig. 34.—*Noncrystalline, nonstriated deposit on under side of horizontal cathode.* × 16

Fig. 35.—*Spiral striae forced from a pure electrolyte by rotation of the cathode, natural size*

Figs. 36, 37, 38.—*Showing that the spacing of the striae is dependent on the cathode curren density; currents 0.044, 0.0075, 0.0010 ampere per sq. cm, respectively* × 5

We were therefore driven to the conclusion that the cause of striæ is something entirely different from what has been suggested, and we made a large number of experiments before we arrived at what we believe to be the true explanation. Before stating our theory of striæ, however, we shall prepare the way by describing some of these experiments, which were for the most part completed before we were aware of the work by Kirmis and Behn. We have confirmed most of Behn's results, but have made many additional experiments of a different character.

C. EXPERIMENTAL FACTS REGARDING STRIATIONS

1. STRIÆ ARE NOT PRODUCED IN PURE SOLUTIONS

We have made hundreds of deposits of silver without filter paper, both in the Richards voltameter and in voltameters without a porous cup, and in no case have we seen striations when the electrolyte was known to be pure. The crystals are distinct, with beautifully developed faces and angles, and no suggestion of striations. But with filter paper as a septum between anode and cathode, or with electrolyte that has been filtered through filter paper, or with the addition of "filter paper extract" or of certain chemicals, striæ are produced more or less distinctly according to circumstances. (Photographs of these shown earlier in this paper.)

2. ONLY CERTAIN KINDS OF IMPURITIES PRODUCE STRIATIONS

Not only filter paper, but linen, cotton, and wood-pulp paper, wood fiber, linen, cotton, and silk textiles, furfuraldehyde, and other strong reducing substances produce striations. The purest of filter paper, which is practically pure cellulose, is effective in producing striations. On the other hand, cane sugar, starch, acids, and a large number of other chemical substances do not produce striations. It is not enough that the electrolyte be impure, but it must contain substances which reduce silver nitrate, as we have explained elsewhere (p. 247), thus producing colloidal silver. This we believe to be the first essential condition for striations.

3. MOTION OF THE ELECTROLYTE OVER THE SURFACE OF THE CATHODE IS NECESSARY

We have confirmed the conclusion of Behn and others that the direction of the striæ is determined by the convection currents of the electrolyte flowing over the surface on which silver is being deposited. The radial striæ on the bottom of the platinum dish (Fig. 6), the parallel vertical striæ on the sides (Fig. 29), the diverging striæ produced where the electrolyte is discharged as a jet upon a cathode surface (Fig. 30), the circular striæ produced on a horizontal cathode in rotation (Fig. 31), the inclined striæ produced on a vertical plate when the electrolyte is given a horizontal motion by rotating the dish containing the electrolyte (Fig. 32), all indicate that the striæ lie along the lines of flow of the electrolyte. On the other hand, if the cathode plate be inclined to the vertical, the striæ are less marked and decrease the more as the inclination to the vertical is greater. (Fig. 33.) When the cathode is horizontal they disappear altogether. (Fig. 34.) Similarly, striæ due to rotation of the vessel, or of a horizontal plate in a stationary electrolyte, are the more pronounced as the speed of rotation is greater. There is thus ample evidence that a motion of the electrolyte over the surface of the cathode is the second essential condition for striations.

4. FORCED STRIÆ IN A PURE ELECTROLYTE

We have stated above that for striæ to appear certain impurities are needed in order to produce colloidal silver in the electrolyte. There is, however, an exception to this statement, namely, where the velocity of the electrolyte is very great. Natural convection currents are sufficient to produce the heaviest of striations when the solution contains considerable of the filter paper impurity. But in a very pure solution, as already stated, not the faintest suggestion of striations is ordinarily seen. However, if a horizontal cathode be rotated in its own plane at a very high speed in a pure electrolyte slight circular striations are produced. (Fig. 35.) The explanation of these forced striæ is in harmony with the explanation of ordinary striæ. (See below.)

5. SPACING OF THE STRIÆ

Striæ are sometimes coarse and far apart and sometimes fine and very close together. It was long ago noticed that variations in the strength of the electric current and of the concentration varied the distinctness of the striæ. Careful observation shows that many deposits which appear unstriated are really very finely striated, but that the striæ have grown together and disappeared. As striæ do not appear at the very beginning of a deposit, and may have appeared and disappeared before the end, it is necessary to look for the striæ during the deposit in cases where they are found very close together. Sometimes they appear at the bend of the bowl near the bottom and not on the sides. This is because the deposit of silver is thinner in the former place, whereas on the sides where the deposit is heavier they have been covered up by the depth of the deposit.

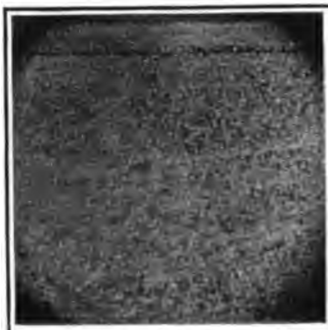
In order to ascertain what determined the spacing of the striæ we made a large number of deposits, varying such conditions as current density, concentration, and temperature, one at a time. In some cases the deposits were photographed and the photographs measured. In other cases the deposits were measured. The spacing does not depend on the degree of impurity, although the distinctness of striation, its microscopic appearance, and its appearance to the unaided eye do depend on the degree and character of the impurity.

6. EFFECT OF VARIATIONS OF CURRENT DENSITY, CONCENTRATION, AND TEMPERATURE

Increasing the current density decreases the distance between striæ. Hence small currents give coarse striæ, heavy currents fine striæ. (See Figs. 36, 37, 38.) The latter are quickly covered up, hence it is sometimes stated that certain current densities give no striæ. Increasing the concentration increases the distance between striæ. Hence weak electrolytes give fine striæ, and stronger electrolytes coarser and more distinct striæ. Increasing the temperature of the electrolyte makes the striæ farther apart. The effect of changes in concentration and temperature may be expressed by saying that increasing the conductivity of the electrolyte increases the distance between striæ.

7. SIZE AND SPACING OF CRYSTALS IN PURE SOLUTIONS

We very early noticed that the size and mean distance apart of the crystals deposited out of pure solutions vary in much the same way as the spacing of the striæ. Sometimes the crystals



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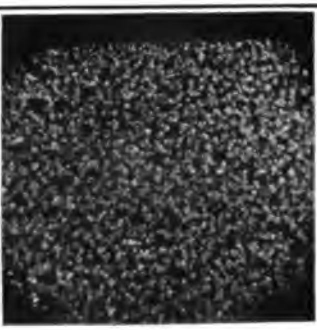

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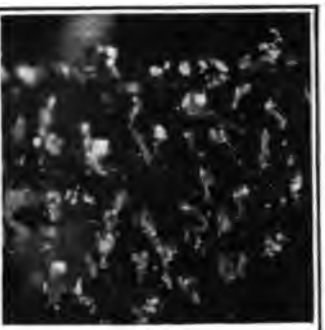

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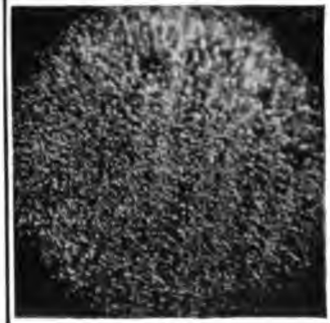

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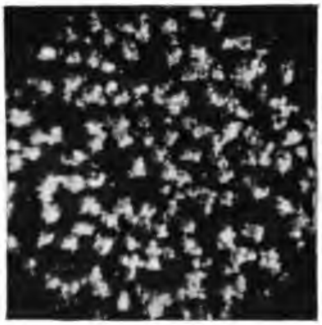

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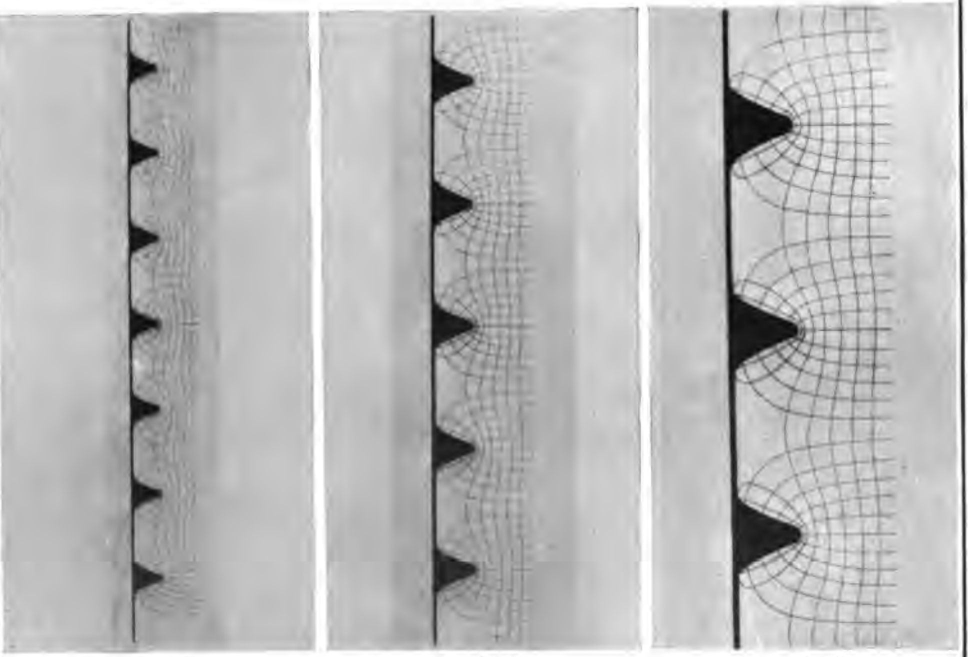


(a) (b) (c)

47

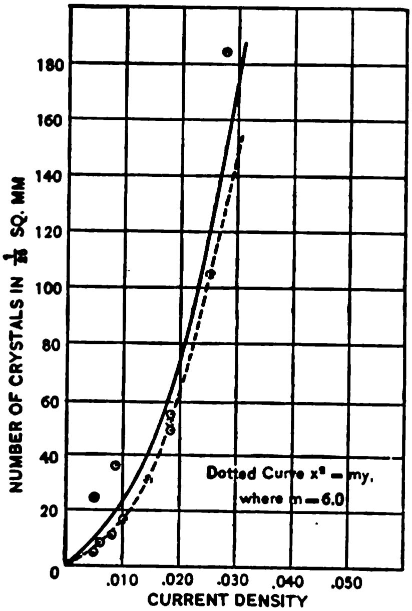
Figs. 39, 40, 41.—*Current density series for pure electrolytes, showing that the size and spacing of the crystals is dependent on the cathode current density, the concentration being the same; currents 0.028, 0.0028, 0.00028 ampere per sq. cm, respectively.* × *5*

Figs. 42, 43.—*Showing that the size and spacing of the crystals is dependent on the concentration of the electrolyte, the current being the same; concentrations 5 per cent, 15 per cent, respectively*

Fig. 45.—*Deposit from a silver nitrate solution to which silver acetate has been added. Showing two kinds of deposit.* × *16*

Fig. 47.—(*a*), (*b*), (*c*), *have been prepared to illustrate tne statements made above respecting the relation between the distance apart of the crystals, the conductivity of the electrolyte, and the density of the electric current. Two equipotential surfaces that lie within the platinum are shown as emerging into the electrolyte around the silver crystal*

are fine and very close together and sometimes they are coarse and relatively far apart, and between these extremes any size or spacing may be obtained by varying the conditions. These conditions are the same as those which determine the spacing of striæ, namely, the current density (see Figs. 39, 40, 41), concentration (see Figs. 42, 43), and temperature. In order to obtain quantitative results a large number of deposits were made in the field of a microscope on a platinum cathode that had been ruled into squares by a fine diamond. The rulings were 0.2 mm apart, so that each square millimeter was divided into 25 equal squares. Thus the crystals could be counted, using a certain current density and time and a definite concentration of the electrolyte. Then the conditions could be varied, and so the relation between these conditions and the number of crystals per unit of area could be determined.



RELATION OF NUMBER OF CRYSTALS TO CURRENT DENSITY. PURE ELECTROLYTE.

Fig. 44

At the start crystals were deposited and a map of a portion of the field made, locating every crystal. Then the cathode was cleaned and the operation was repeated a number of times. This was to see whether crystals always appeared at the same places. There were of course in the surface of the platinum plate minute scratches and irregularities which under the microscope were plainly visible, and although sometimes the crystals would be seen lying along a scratch like beads on a string, generally their distribution was quite independent of any such markings and quite independent of the straight lines ruled by the diamond on the platinum cathode. No two distributions of crystals over a given area were alike, and we noted no points or spots where crystals tended to appear repeatedly by preference.

With a variation of current density the number of crystals is approximately proportional to the square of the current density. Fig. 44 gives the results of some measurements. Thus with small current density the crystals would be large and relatively few; with large current density the crystals are small and more numerous, the total quantity of silver deposited being the same in each case. With increasing concentration the crystals are larger and fewer, and so also with increasing temperature. That is, increasing the conductivity of the solution increases the distance between crystals (as it does between striæ) and increases the size of the crystals. As the size of the crystals is inversely proportional to their number, and their mean distance apart is inversely proportional to the square root of their number, we see that the mean distance apart of the crystals is approximately inversely proportional to the current density. Photographs of deposits under different conditions illustrating these facts are shown in Figs. 39, 40, and 41.

8. EFFECT OF ACID AND ACETATE

A trace of acid in the electrolyte makes the crystals finer, and hence gives the deposit a different appearance, but does not produce striations. For a given total weight of silver deposited the average size of crystal is of course inversely proportional to the number. The number of crystals is determined the first moment of the deposit. Thereafter they increase in size quite uniformly, except that if the deposit continues a considerable time they grow together in many cases, so that the number decreases and the variation in size is accentuated. Very few new crystals start after the first instant, unless the current is considerably increased.

A trace of silver acetate dissolved in the silver nitrate makes the crystals *very* fine—that is to say, starts the crystals very close together and in great numbers. Thus the platinum surface becomes covered by a more or less continuous deposit, which under the microscope looks like a surface of frozen snow. The crystalline deposit from the pure nitrate, on the other hand, consists of a great many relatively large and separate crystals, with large areas of bare platinum between. The contrast is very striking.

In addition to the white deposit of fine crystalline silver, in the case of the solution containing silver acetate, there is present when filter paper has been used (or filter paper extract) a black deposit of silver which we believe has been laid down from the colloidal condition, but which on heating turns first yellow and then white. (Fig. 45.) It is readily distinguished under the microscope from the normal silver deposit, and its presence makes the weight of silver too heavy. The silver acetate is more easily broken down by the reducing agents (chiefly furfuraldehyde) formed from the cellulose of the filter paper, and so increases the weight of the deposit much more than when the silver acetate is not present.

9. VELOCITY OF THE CONVECTION CURRENTS

We have stated that we believe the motion of the electrolyte over the cathode is one of the essential conditions for the production of striæ. These convection currents can be seen in a voltameter with glass sides, since the variation of the density of the electrolyte between the anode and the cathode is considerable. By the aid of the microscope and ruled cathode plate employed in counting the crystals we succeeded in measuring approximately the relative velocity of these convection currents under different conditions. Using a small voltameter with parallel glass sides, the cathode plate was vertical, and the microscope was focused on the plate. Small particles of the anode slime which became detached from the anode circulated around with the convection currents, and served as an index of its velocity. Of course, the velocity of the liquid was different at different distances from the cathode, but by focusing on the plate tiny particles even a short distance away could not be seen distinctly. Thus we observed the sharply defined particles falling in the field (they were rising in reality) at a uniform rate, and by timing them with a stop watch as they crossed the horizontal lines ruled on the cathode their speed was measured with fair accuracy. The speed varied with the density of the electric current, as would be expected, increasing with greater current. The speeds observed (Fig. 46) varied from 0.1 mm per second to 0.7 mm per second,[47] using concentrations and current densities such as are used in practice. Probably in larger voltameters the speed would be greater.

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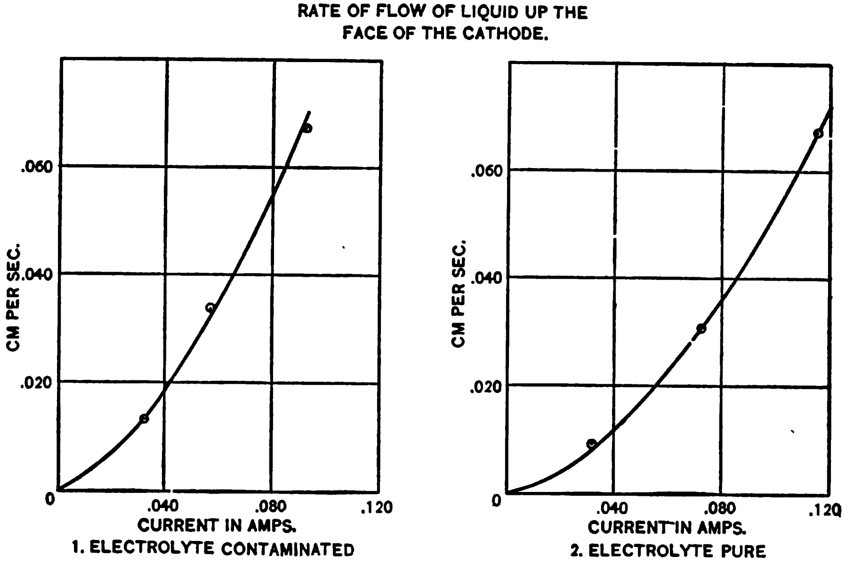
[47] This is much less than the estimate given by Smith, Mather, and Lowry, namely, 1 cm per second. However, their estimate was based on the inclination of striæ and was not a direct measurement.



1. ELECTROLYTE CONTAMINATED

2. ELECTROLYTE PURE

Fig. 46.—*Curves showing the rate of flow of liquid up the face of the cathode as dependent on the current*

D. THEORY OF DISCONTINUOUS DEPOSITS

We have described the deposits of silver from pure solutions of silver nitrate as invariably crystalline, the bare platinum cathode being plainly visible between the crystals; from impure solutions it appears noncrystalline, but a microscope shows the irregular masses of silver to be aggregates of fine crystals. In neither case is the cathode completely covered. On the other hand, the deposits from a solution of cyanide of silver appear perfectly continuous even under a very high magnifying power, and are therefore radically different from the deposits from the nitrate.

It is an interesting and important question to determine *why* the crystals are deposited in the manner described above, and why the current is concentrated into the silver crystals initially started, instead of spreading out over the surface of the platinum as it does when a solution of cyanide of silver is used. It is a striking phenomenon to see the area of bare platinum on the cathode surface of a silver voltameter, a thousand times greater than the area of the silver crystals, in the early stages of the deposit, and yet no current flowing to the platinum surface, but only to the tiny silver crystals. As Ohm's law holds in the electrolyte, it is evident that there is at the surface of the platinum *a potential difference opposing the current, which brings the electrolyte in contact with the platinum to a higher potential than that of the electrolyte in contact with the silver*, and so the current is turned away from the platinum surface, finding numerous outlets to the platinum cathode through the silver crystals. It is as though the potential difference at the start breaks through the surface film (which offers a counter electromotive force) at numerous points, and these initial outlets, which increase in area as the crystals grow, are sufficient, unless the current density is suddenly increased.

The surface potential differences taken in connection with the specific resistance of the electrolyte and the current density determine the distance apart of the crystals. In a very concentrated solution the specific resistance is less, and hence the fall of potential corresponding to the surface differences of potential occurs in a greater distance. Hence the crystals will be farther apart than in a normal solution. On the other hand, in a very weak solution of higher specific resistance the fall of potential is steeper and hence the given potential difference will occur in a shorter distance. Hence the crystals will be nearer together and more numerous, and hence also the crystals very small. Heating the solution increases its conductivity, and therefore has the same effect as increasing the concentration; that is, the crystals are further apart and of larger size. (See Fig. 47.)

We have attempted to develop this theory of surface potentials to explain the form of electrolytic deposits from other silver salts and salts of other metals, and have had some success in doing so, but we found ourselves getting so far away from the problems of the silver voltameter that we abandoned that work for the present and returned to the question which directly concerned the silver voltameter.

E. EXPLANATION OF STRIATIONS

After having given this question careful study, we offer the following explanation, which we believe is in accord with the known facts regarding striæ.

In the first place it should be remembered that silver crystallizes according to the cubical system, and when deposited out of a pure solution of silver nitrate various modifications of cubical crystals are formed, as octagonal, dodecehedral, etc., in addition to cubes and rectangular parallelopipeds. These crystals are formed more perfectly in very pure solutions, and deposits examined under a binocular microscope show beautifully the perfect faces and angles of these various geometrical forms. Slightly impure solutions have their crystalline forms greatly modified, aggregates of needle-shaped crystals predominating in deposits made from solutions slightly contaminated by filter paper. As the impurity increases, the crystalline character disappears, the deposits being masses that often look like molten metal, cinders, or slag. High magnification shows that such deposits are made up of aggregates of very small crystals. The regular crystalline growth that takes place normally in electrolytic deposits from a pure solution of silver nitrate, whereby large crystals are built up, can not occur when the solution is strongly contaminated by filter paper or other forms of cellulose, or by furfuraldehyde.

The reason why a regular crystalline growth does not occur when filter paper extract is present is, we believe, that colloidal silver is produced by the reaction of furfuraldehyde (produced from oxycelluloses) on silver nitrate and that this colloidal silver is deposited on the silver and breaks up the regular growth of the crystals, each particle probably serving as a nucleus for a new crystal. Thus the deposit in such cases is an aggregate of very small crystals instead of relatively large crystals.

When the current starts the deposit begins at many isolated points, the distance between crystals being hundreds of times the linear dimensions of the crystals themselves at the end of the first few seconds. The stream lines along which the current flows are thus concentrated at the cathode end, upon these incipient crystals, no current flowing to the bare platinum after the first instant. The upward current of liquid along the crystal surface (due to the smaller density of the impoverished electrolyte at the cathode) carries the chain of ions which lie along a given stream line upward out of its normal course, so that the current tends to reach the upper surface of a crystal. We must suppose that in a pure electrolyte the force of crystallization constrains the silver atoms to be deposited in regular order, thus building up, as we know, crystals of relatively large size, in spite of the tendency of the convection currents in the liquid to distort the crystals by building them upward. For we find the same regularity of crystalline growth on the vertical sides of a cathode vessel as on or near the bottom. But in an impure solution the regular crystalline growth is interfered with by the deposit upon the initial crystals of particles of colloidal silver. Thus, as new crystals are started at every point where a particle of colloidal silver has been deposited, the silver grows by preference upward in the direction favored by the upward movement of the liquid. Watching this process under the microscope one sees the small crystals which appear at the start grow upward so that after a time instead of a large number of silver crystals of approximately equal dimensions in different directions one sees a great number of elongated deposits, the longest dimension being vertical. These tend to grow into one another, so that after a time striations have developed, that is, there are ridges of silver of more or less equal distance apart, separated by intervals of bare platinum.

The striation can not even be suspected at the start, but after a time it becomes well marked, and then if the deposit is continued long enough the ridges of silver growing in width join together, the platinum surface is gradually covered, and the striation finally disappears.

If the current density is relatively small at the start, the initial points of deposit are comparatively far apart, and when they have become elongated vertically and joined together more or less they form striæ, which will be comparatively wide apart. On the other hand, if the current density be larger, the points of deposit initially will be more numerous, and the striæ will be closer together. Observation shows that the number of striae per centimeter is approximately proportional to the current density, or the distance between striæ is inversely proportional to the current density. In the same way, the initial distance between crystals (in a nonstriated deposit) is inversely proportional to the current density, or the number of crystals per square centimeter is proportional to the square of the current density. This explains why a small current gives coarser crystals than a larger current for a given weight of deposit, for doubling the current multiplies the number of crystals by four, and hence reduces the average weight of each crystal to one-half. The original incipient crystals appear in the field of the microscope almost at once, perhaps within a second or two after closing the circuit. They are so tiny when first seen that millions would be required to weigh a milligram, and as they grow larger they amalgamate more or less, so that the number of separate crystals decreases.

Adding a trace of acid changes the potential difference at the surface of the platinum in such a way as to make the crystals nearer together and hence more numerous and smaller in size for the same weight of deposit.

We have spoken above of an exception to the general rule regarding striæ in what we call forced striæ. If a cathode be rotated at a moderate speed in a pure electrolyte, no evidence of striation appears, but if the speed of rotation be increased there is a slight circular striation, although the deposit is crystalline. The high speed constrains the crystals to grow in the direction of motion, for the same reason as in an impure deposit, except that it requires a much higher speed in the pure solution. The result is, however, radically different in the two cases, the deposit in the case of the pure solution where the speed of the electrolyte over the cathode is high being crystalline and only slightly striated. This case of forced striæ in a pure solution is thus quite in harmony with the explanation here offered for normal striæ.

This paper is to be followed by two more, of which the first will deal with the quantitative experiments preliminary to the meeting of the International Technical Committee and will also contain a discussion of the purification and testing of silver nitrate. The final paper will deal chiefly with the determination of the voltage of the Weston normal cell and the question of specifications for the voltameter.

WASHINGTON, October 1, 1912.

THE DIFFUSE REFLECTING POWER OF VARIOUS SUBSTANCES[1]

By W. W. Coblentz

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I. INTRODUCTION

In all radiometric work involving the measurement of radiant energy in absolute value it is necessary to use an instrument that intercepts or absorbs all the incident radiations; or if that is impracticable, it is necessary to know the amount that is not absorbed. The instruments used for intercepting and absorbing radiant energy are usually constructed in the form of conical-shaped cavities which are blackened with lampblack, the expectation being that, after successive reflections within the cavity, the amount of energy lost by passing out through the opening is reduced to a negligible value.

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[1] This title is used in order to distinguish the reflection of matte surfaces from the (regular) reflection of polished surfaces. The paper gives also data on the specular reflection of polished silver for different angles of incidence, but it seemed unnecessary to include it in the title.

A simpler and older form of radiometer is a plane surface covered with an absorbing substance. In this case it is necessary to determine the amount of energy lost by reflection from the surface of the receiver. If the blackened receiving surface is small, it may be placed at the center of curvature of a hemispherical mirror, the the radiant energy being admitted through a hole in the center of the mirror. The receiver being at the center of curvature of the mirror, any radiations which are diffusively reflected from the receiver will impinge upon the mirror and will return to the receiver. The amount of energy lost by returning upon its path through the opening in the mirror can be determined experimentally.

The most useful substances for absorbing radiant energy are lampblack and platinum black. The present research was undertaken in order to establish methods for the production of standard absorbing surfaces from standard materials, and to determine the completeness of the absorption (i. e., the amount lost by diffuse reflection) of these substances in different regions of the spectrum.

The reverse problem was also presented, of finding a "white" surface, which absorbs the least radiation (high reflection) in the visible and in the adjoining infra-red part of the spectrum, and which has a low reflection in the region of 8 to 9 μ. Such a surface would absorb but little sunlight, and it would not become heated by the part that is absorbed, owing to reradiation, which is facilitated by the high emissivity in the region of 8 to 9 μ, where occurs the maximum radiation of substances having a temperature of 20° to 50° C.

Expressed in a more popular way, the interest in the present research was in finding substances having the extremes in diffuse reflection; i. e., the whitest "white" and the blackest "black," the former to be used as a paint (which will absorb but little of the sun's rays) to cover a building (e. g., an observatory dome) which is to contain instruments that are sensitive to changes in temperature, the latter to be used as the absorbing surface of a radiometer which is located within this building.

While it is beyond the scope of the present investigation to discuss the theoretical aspects of this subject, it is of interest to notice the extraordinary and apparently inconsistent ways in which these extremes in diffuse reflection are produced. In optically transparent media (insulators), such as glass, the absorption coefficient and the refractive index are low and the amount reflected regularly ("vitreous reflection") is of the order of 4 to 5 per cent. On the other hand, in the metals (electrical conductors), such as platinum, the absorption coefficient and the refractive index are high and the amount reflected regularly ("specular reflection") is of the order of 80 to 100 per cent, depending upon the wave length. On first consideration it therefore seems somewhat contrary to the natural order of things to produce a high (90 per cent) reflecting (diffuse reflection) surface from the former and an extremely low (1.5 per cent) reflecting surface from the latter by merely changing the size of the grains which form the reflecting layer.

The high reflecting power of fine particles of transparent substances (insulators) is easily explained as the result of successive internal reflections and refractions of the light which penetrates their surfaces. If the particles are small, the chances are that total reflection will occur before the rays have penetrated to a great depth, and (there being practically no absorption) the rays are reflected with almost the same intensity as obtained in the incident radiations.

When the reflecting particles have a high absorptivity but have a low refractive index, which is true of lampblack, the same optical conditions obtain as in the more transparent particles, the only difference being that at each internal reflection the rays are further absorbed so that the intensity of the reflected rays is quickly reduced to a small value in comparison with the incident rays. The blackest deposits of soot are made by holding a metal plate in an acetylene flame, which forms an extremely fine-grained surface. Such a deposit, viewed at grazing emergence, has the appearance of a highly polished mirror of fairly high reflecting power.

The effect of grain size upon the amount of energy (diffusively) reflected from the surface is well illustrated in the present paper, which gives the reflecting power of a cleavage surface and of a coarsely ground surface of white marble. The cleavage piece (about 1 cm thick) was well illuminated throughout the interior, to the rear surface, owing to the large size of the individual crystals, some of which had cleavage faces 0.2 to 0.3 mm diameter.

The low reflecting power obtained by reducing the size of metallic particles (e. g., platinum black) to the dimensions of light waves is not so easily explained. If the black mass is a coagulation of colloidal metal, its optical properties (refractive index, etc.) are the same as that of the metal.[2]

Evidently it is not a question of roughness of surface, for a deposit of platinum black (upon a strip of platinum) when heated to a low red heat sinters into a white mass. By eliminating the high reflecting power platinum could become black by assuming a structure of fine particles, which consists of cavities with small openings. Such a condition would be realized if the material had the structure of a bundle of polished needles,[3] turned with their points toward the light. By multiple reflection the rays will travel down into the interstices between the needles (particles forming the spongy mass) and practically none will escape by reflection back upon their path. It is conceivable that by electrolysis the platinum black might be deposited in isolated points with relatively large spaces intervening, and that, as the electrolysis continues these points increase in height and diameter, thus forming a porous needle-shaped structure. This would increase the absorption of electrolytically deposited platinum black (as observed), but it does not fully explain the physical condition of the chemically precipitated material, unless we assume that the latter, which is colloidal, was built up in a similar manner by coagulation.

A more plausible explanation, alluded to by Kurlbaum,[3] is based upon the depth of penetration of the rays into the metal and the thickness of the reflecting layer. In order to obtain reflection a definite thickness of metal is required, which thickness is a function of the wave length of the incident light. Hagen and Rubens[4] determined the reflecting power of gold with thickness on the assumption that the layer is homogenous, i. e., not formed of discrete particles with intervening spaces of glass. They found that for a layer 0.01 μ in thickness the amount of light reflected was about 10 per cent of the total reflecting power for that wave length. The maximum thickness required for complete reflection of all wave lengths was about 0.08 μ. The smallest particle of colloidal material, e. g., gold, observable in a microscope is of the order of 0.01 μ.[5] It is conceivable that there are colloidal particles which are still smaller, and that platinum black is made up of aggregations of these invisible particles. In this case it is conceivable that, if the thickness of the particle is less than the minimum thickness required in the transition layer to obtain reflection, then the rays will pass through the particle, diminished in intensity by the amount absorbed in the particle. This is the somewhat elaborated view taken by Kurlbaum (loc. cit.), who based his line of argument upon Stark's[6] investigations of the physical properties of soot. In a deposit of soot Stark considered the air a turbid medium containing the particles of soot.

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[2] Spence: Phys. Rev., **28**, p. 233; 1909.

[3] Kurlbaum: Ann. der Phys. (3), **67**, p. 855; 1899. Wood: Physical Optics, new ed., p. 449, Absorption by Porous Surfaces.

[4] Hagen and Rubens: Ann. der Phys. (4), 8, p. 432; 1902.

Owing to the high absorption coefficient of metals the rays should therefore be completely absorbed in a thinner layer than is required in lampblack. Kurlbaum found that about 3.5 times as much (by weight) platinum black was required to produce the same absorption as in soot. Evidently not all of the individual particles of platinum black are of the minimum thickness required to avoid reflection or the material has some property as yet unknown. This is inferred on the assumption that the density and the thickness of the layer of these two materials is the same in the experiment, which was not the case. Evidently further investigations are necessary to decide these questions.

In the foregoing paragraphs we have noticed the most probable causes which are instrumental in producing these two extremes in diffuse reflection. In view of the fact that many of the insulators (optically transparent media, for the visible spectrum) have two types of absorption (reflection) bands in the infra-red, which sometimes fall within the spectral regions examined in the present investigation, it is important to notice the distinction between these two types of bands. For example, a plate of quartz is transparent to the visible spectrum, has absorption bands in the region of 4 μ, and a band of metallic reflection (of about 90 per cent) in the region of 9 μ. The apparently anomalous condition of a high (diffuse) reflection of the powder in the visible and at 8.8 μ and a low reflection at 4.4 μ is therefore easily explained; for in the region of 4.4 μ the surface permits the formation of "body color," as is true of pigments.[7] In the region of 8.8 μ the high reflection in powdered quartz is owing to the coarseness of the grains. If the grains were as fine as those of platinum black, one would expect the reflecting power in this spectral region to be as low as obtains in platinum black. Similar conditions are to be observed in some of the pigments, e. g., litharge, yttrium oxide, and chromium oxide.

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[5] Burton: Phil. Mag., 2, p. 425; 1906. Spence: Phys. Rev., 28, p. 233; 1909.

[6] Stark: Ann. der Phys. (3), 62, p. 353; 1897.

II. SUMMARY OF PREVIOUS INVESTIGATIONS

Three methods have heretofore been used in determining the amount of energy lost by diffuse reflection from rough surfaces. The first method is based upon the assumption that the diffusion follows the cosine law. The amount of incident energy is measured; also the amount of energy reflected at a given angle from the normal. By integration the total amount is obtained that is lost by diffuse reflection. This method was used by Ångström.[8] He used a surface bolometer at an angle of 40°, and found that for a thickly sooted platinum black surface the reflecting power varied from 0.82 per cent to 1.25 per cent, being apparently larger for the short wave lengths. Practically the same method was used by Hutchins.[9] With a radiomicrometer he investigated the cosine law of diffuse reflection of various substances. He found that the diffusion from rough surfaces of such substances as magnesium oxide and plaster departed an appreciable amount from the cosine law, for large angles, while for paper this departure was very marked for angles between 20° and 60°. By integration he found the total amount of energy lost by diffusion.

For a white surface, "plaster," using sunlight as a source of energy, the integrated value for the reflecting power (the albedo) was 92.7, for paper it was 82.6, and for a green leaf it was 30.2, which values are in fair agreement with the results of the present research.

Another method for obtaining the diffuse reflecting (the absorbing) power is to compare the emission of a heated surface with the emission of a black body which is at the same temperature. This method was used by Crova and Compan.[10] They found that the loss by reflection from the soot of a candle flame varied from 0.68 to 1.25 per cent, and for a layer of the same washed with alcohol the loss was 3.17 per cent. Kurlbaum[11] used this method to find the absorption (emission) of different thicknesses of electrolytically deposited platinum black and of soot. For soot the maximum emission of 94.5 per cent was attained in a deposit containing about 30 mg per dm ^{2}; but using a thicker deposit of about 100 mg per dm ^{2}, the emission was only about 88 per cent of that of a black body. For platinum black the emission was only about 30 per cent for a deposit weighing 30 mg per dm ^{2}. The maximum emission of 96.8 per cent was attained in deposits weighing about 200 mg per dm ^{2}, which value remained constant for deposits weighing 300 mg per dm ^{2}.

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[7] See Wood's Physical Optics, new ed., pp. 441 and 439, Body Color and Surface Color.

[8] Ångström: Öfversight Af. K. Vetensk. Akad. Förhandlinger, Stockholm, 55 (No. 5), p. 283; 1898. Wied: Ann. der Phys. (3), 26, p. 253; 1885.

[9] Hutchins: Amer. J. Sci., 6, p. 373; 1898.

He recommended that for measuring radiations of wave lengths up to 8 μ it is sufficient to deposit the platinum black for three minutes, using the current density and concentration of solution, etc., described on a subsequent page. According to the present method of investigation, in which the platinum black was produced by the same formula as used by Kurlbaum, the deposition of platinum black should be continued for five to six minutes.

The main objection to this method is that it gives values for the complete spectrum.

A third method is to place the reflecting substance and a radiometer at the conjugate foci of a hemispherical mirror. The incident radiation is introduced upon the reflecting substance by passing through a hole in the center of the mirror. This method is the easiest to employ, but it requires the determination of several correction factors, which, however, are constant quantities in the investigation. These corrections are (1) the amount of radiation which escapes through the opening in the mirror, and (2) the amount of diffuse radiation, which, in its course from the reflecting substance to the radiometer, is absorbed by the silver mirror.

Using this method Royds[12] carried out a series of measurements under the direction of Paschen. In view of the fact that the present research was well under way when the results of Royds were published, and that the methods differ only in minor yet important points (the results being at considerable variance), it is of interest to notice this work in some detail.

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[10] Crova and Compan: Compt. Rend., **126**, p. 707; 1898.

[11] Kurlbaum: Ann. der Phys. (3), **67**, p. 846; 1899.

[12] Royds: Phil. Mag., **21**, p. 167; 1911. Phys. Zs., **11**, p. 316; 1910.

Royds used a hemispherical mirror of German silver 5 cm in diameter. The Rubens thermopile and the blackened strip were placed side by side in the focus of the mirror and the incident energy (the image of an illuminated slit) was projected on either the strip or the thermopile by means of an external concave mirror. The thermopile did not present a completely opaque surface to the incident radiations and hence a great amount of the available energy could not be utilized. Moreover, the slit image after reflection from the diffusing surface may not be very sharp and it may not be uniformly illuminated. This is very marked in the transparent, "white," substances, in which much of the light is reflected at considerable distance below the surface so that the observations must be made upon the assumption that the distribution of the radiation (the "illumination") is the same in the slit image before and after reflection from the diffusing surface. This uniformity of illumination is probably of minor importance for black surfaces, but it is of considerable importance with white surfaces which may reflect as high as 90 per cent of the incident energy. Royds makes no mention of having tested his outfit with a white diffusing surface, e. g., magnesium carbonate, which gives a surprising amount of information in regard to the adjustments, the distortion and illumination in the slit image, etc.

Since the thermopile and the reflecting surface were stationary and the image of the illuminated slit was projected upon either one by means of an external concave mirror the arrangement of the apparatus did not permit the use of a cone of rays which filled the opening in the hemispherical mirror. This resulted in a further reduction of the available incident energy, so that in order to be able to measure the small amount of energy which is reflected from lampblack, a very sensitive ($i=0.7\times10^{-10}$ amp.) galvanometer had to be employed. As a result he had to apply corrections for diffuse radiation from the incident image, and for energy radiated from the black surfaces as a result of warming from exposure to the incident radiation. No corrections were made for absorption by the mirror nor for the opening in the mirror, which correction he says could not be estimated. The various corrections to his observations were such that his "apparent" values are two to three times his "true" values. His "apparent" values are usually in fair agreement with results obtained in the present paper. He examined the spectral regions of 0.95, 8.8, 25, and 52 μ, but owing to the great impurity of the radiations in the last two spectral regions the observations can not be given much weight.

III. APPARATUS AND METHODS

In designing the present apparatus the attempt was made to utilize the maximum amount of the available energy. This permitted the employment of a galvanometer of low sensitivity, which eliminated such corrections as necessarily result when using a very sensitive radiometer. For example, the correction used by Royds for the diffuse energy falling upon the thermopile caused by the reflection from air particles when the incident radiation is directed upon the lampblack was nil in the present investigation. The utilization of a large amount of the available incident energy resulted from (1) the employment of a large hemispherical mirror which permitted the use of a large incident slit image and a large reflecting surface without distortion; (2) the use of a radiometer which intercepted the whole slit image; (3) the use of a beam of radiations which filled the opening in the hemispherical mirror, which was made possible by shifting the thermopile and the diffusing surface instead of shifting the slit image, as was done by Royds. The main objection to moving the thermopile from its position at the conjugate focus of the reflecting surface, *p*, Fig. 1, *A*, to the position, *c*, occupied by the reflecting surface, which is necessary in order to determine the intensity of the incident radiation, is the shift of the galvanometer reading owing to differences in emissivity and in temperature in the two positions. This is not marked, however, at the low galvanometer sensitivities used in the work.

The apparatus resulting from the foregoing considerations proved far more sensitive than was expected, so that for all spectral regions investigated (excepting at 24 μ) the galvanometer,[13] of 5.09 ohms resistance, was used on a complete period of two to three seconds and a sensitivity of about 1×10^{-9} ampere. For the spectral region of 24 μ the complete period of the galvanometer was from four to five seconds, the corresponding sensitivity being about 4×10^{-10} ampere.

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[13] This Bulletin, 9, p. 7; 1912.

The ability to use a short-period galvanometer afforded a great saving in time. In fact, the time was consumed mainly in waiting for the optical system to come to temperature equilibrium after mounting a specimen in the hemispherical mirror. This, however, was not a serious matter, owing to the low radiation sensitivity required in the work.

1. The Thermopile.—The thermopile consisted of 22 junctions of bismuth and silver [13] mounted in a space 10.5 mm long, as shown at *p*, Fig. 1, *A*, and Fig. 1, *E*. Its width was 5 mm and its resistance was 10.8 ohms. The individual junctions were made of bismuth wire 0.1 mm in diameter and silver wire 0.0513 mm diameter, mounted upon an ivory support, *i*, as shown in Fig. 1, *E*. The wires leading to the galvanometer are attached to the binding posts *b b*, Fig. 1. The thermopile was blackened with a mixture of lampblack and platinum black, then smoked with soot from a sperm candle. It was covered with a sheet of glass 0.095 mm in thickness, for observations in the spectral region to 0.95 μ; and with a plate of clear rock salt 0.8 mm in thickness for the longer wave lengths. The use of a receiver that intercepted the whole slit image eliminated the question of distortion and uniformity of illumination. In the incident slit image the rays are received in practically a normal direction upon the thermopile. In the slit image, formed from the rays reflected from the diffusing surface, the rays fall upon the thermopile at all angles of incidence. The only assumption which is made is that the difference in the loss by reflection from the thermopile and the window is negligible in these two measurements.

2. The Hemispherical Mirror.—The diameter of the hemispherical mirror, which was made of glass, was 10 cm, and the opening for admitting radiation upon the thermopile was 10 by 20 mm.

The arrangement of the mirror in the mounting is shown in Fig. 1, *B*. The support for the thermopile and the substance to be investigated was mounted upon a movable stage, *d*, *S*, which in turn was mounted upon a brass plate, which was provided

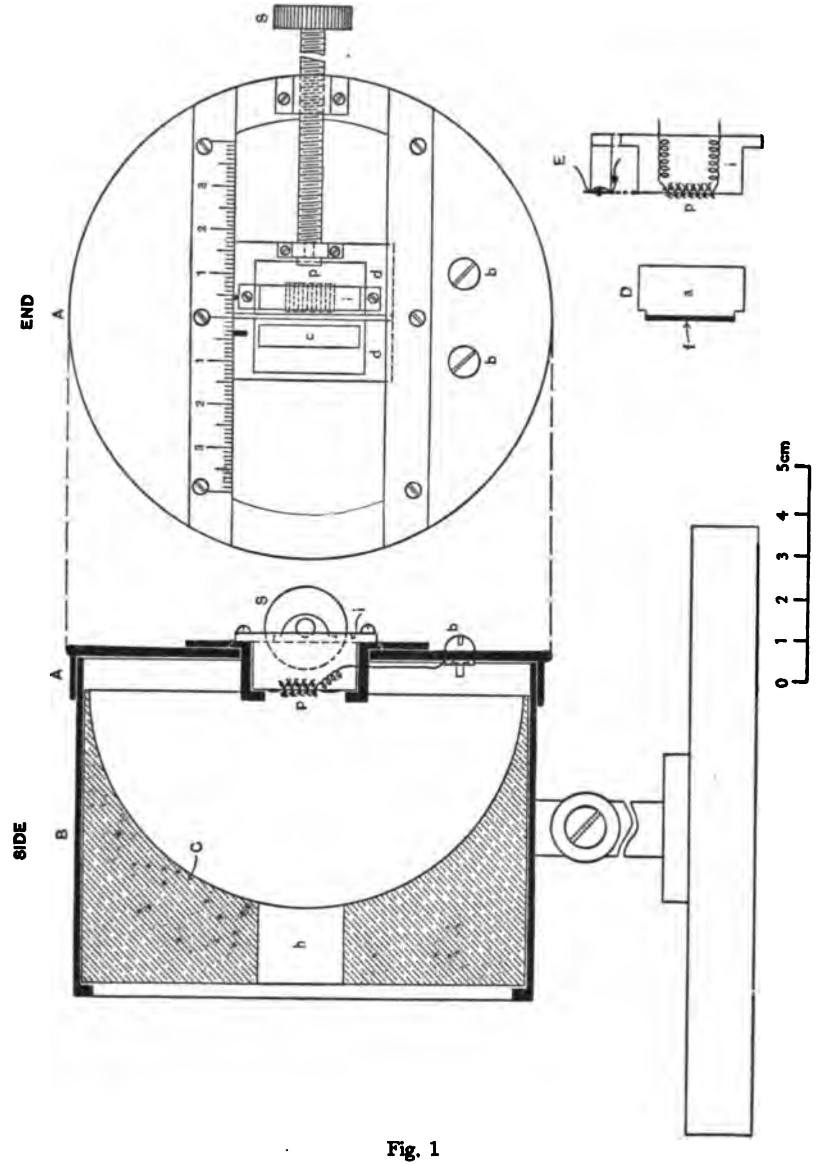

Fig. 1

with a wide flange, Fig. 1, *A*. By slightly tilting this brass plate, *A*, upon the support, *B*, it was possible to focus the slit image of the radiations reflected from the diffusing surface, *f*, Fig. 1, *D*, upon the thermopile, *p*. This adjustment of focus was necessary for specimens which did not fit nicely in the place occupied by the brass block, *a*, upon which the substances, *f*, were usually mounted.

The distance (6 to 7 mm) between the centers of the incident slit image (falling upon the surface, *c*) and its reflected image upon the thermopile, *p*, Fig. 1, *A*, was made as small as possible in comparison with the size of the hemispherical mirror. Previous tests with a Nernst glower 10 mm long showed no distortion of the image of the glower for a displacement of 1.2 cm from the axis of the mirror. However, in the slit image of the light reflected from the diffusing surface the illumination did not appear so uniform, and there appeared to be more abberation at the ends of the slit image. This was especially marked in a cleaveage piece of marble, from which the reflected slit image was surrounded with a hazy illumination. A piece of white cardboard with an opening 5 by 10 mm was placed over the thermopile. This facilitated in focusing and in determining that all the diffusely reflected light fell upon the thermopile.

These adjustments were made with a white diffusing surface (of Al_2O_3 of $PbCO_3$) of the same thickness as the lampblack surfaces, which, owing to its high reflecting power, produced a bright slit image. In this manner the effect of change in focus upon the amount of radiation falling upon the thermopile was investigated.

3. **The Optical System.**—The arrangement of the optical parts of the auxiliary apparatus is shown in Fig. 2, which shows the hemispherical mirror, *A*, containing the reflecting substance, *f*, and the thermopile, *p*. The cylindrical acetylene flame was at *a* and the Bunsen flame, or Welsbach mantle, was at *b*. The shutters, *d* and *e*, were made of thin sheet aluminum (10 by 15 cm), with an intervening layer of asbestos about 3 mm in thickness. They were bright on the front side and painted black on the side toward the thermopile. A large water-cooled diaphragm, with an opening 5 cm in diameter, was placed at *C*, and all of the apparatus to the right of *C*, Fig. 2, was inclosed to exclude stray light. A flame placed back of a large plate of sheet iron with a slit, *s*,

represented the source of energy. An image of this slit was projected into the hemispherical mirror by means of a large concave mirror, *B* (17 cm diameter, 100 cm focal length), or by means of a triple achromatic lens, *L*, having a diameter of 6 cm and a focal length of 18 cm. In the latter arrangement, which was used in the first observations at 0.6, μ the slit, *s*, and flame, *a*, were of course placed on the axis of the lens, *L*.

The arrangement of the two flames, *a* and *b*, the concave mirror, *B*, and the plane, silver on glass, mirror, *M* (with or without an absorption cell, *c*), as shown in Fig. 2, permitted the measurement of the radiations at 0.60, 0.95, and 4.4 μ in succession before changing a specimen. For isolating the radiations at 8.8 μ two quartz plates, 5 mm in thickness (ground and blackened on the rear side) and the silver mirror, *M'*, were placed as shown at Q_1 and Q_2. Two fluorite plates were placed at Q_1 and Q_2, respectively, for isolating the radiations at 24 μ. The proper positions of these mirrors were obtained by focusing with silver on glass mirrors at Q_1 and Q_2, respectively.

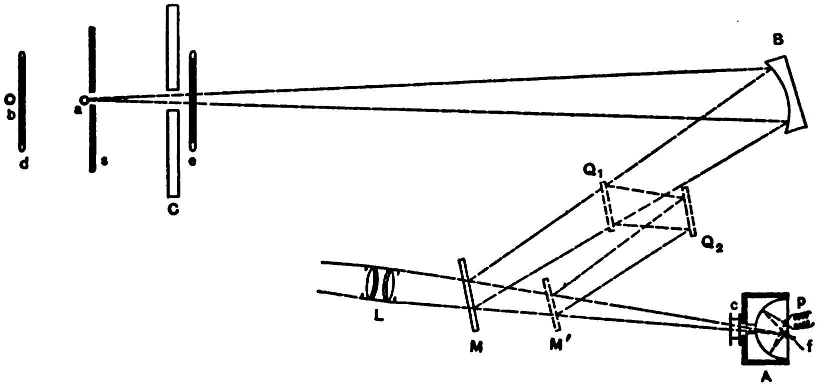

Fig. 2

The beam of light did not entirely fill the opening, *h*, in the hemispherical mirror, so that by slightly turning the mirror, *B*, about a vertical axis it was possible to change the angle of incidence of the radiations and project them upon different parts of the reflecting surface, *f*, which usually was about 6 mm wide and from 12 to 20 mm in length.

The material to be examined was usually mounted upon a brass block, *a*, Fig. 1, *D*, which was 25 by 6 by 10 mm, which was inserted in the opening, *c*, in the stage, *d*, Fig. 1.

The arrangement of the shutter, *d*, and the gas mantle, *b*, at a distance of about 15 cm from the slit, *s*, Fig. 2, prevented the latter from becoming warm and radiating upon the thermopile which would happen when the water cell, *c*, was not in place. When the gas mantle or the Bunsen flame were used (for radiations at and beyond 4.4 μ) the acetylene flame was of course extinguished, the shutter, *e*, was kept raised, and the absorption cell, *c*, was removed.

When using the triple achromatic lens for projecting the slit image, the size of the opening in the sheet of metal, *s*, which formed this slit was 1.5 by 7.5 mm and the image was practically the same size. Owing to the large angle of incidence there was some astigmatism in the image produced by the concave mirror. The slit was therefore reduced to 7 by 2 mm and finally to 7 by 1.5 mm. In all cases the image of the slit at *f* was about 8 by 2 mm, hence there was no danger of the radiations falling outside of the thermopile, especially after reflection at *f* and refocusing at *p*, Fig. 2, when the slit image was not very sharp.

The method of determining the reflecting power consisted in observing the galvanometer deflection when the radiations were projected upon the specimen at *f*, and after reflection therefrom were focused upon the thermopile at *p*; then, moving the stage, *s*, Fig. 1, until the thermopile occupies the position of *f*, observing the galvanometer deflection for the direct slit image. The ratio of the reflected radiations to the direct radiations (in galvanometer deflections) gives the reflecting power. The observations were duplicated for most of the substances. This is especially true for the radiations at 0.65 μ where the triple achromatic lens and also the concave-mirror arrangement were used for projecting an image of the slit upon the substance; also for the radiations at 0.95 and 4.4 μ, using the concave mirror for projecting the slit image. In the final work many of the original observations were repeated at 0.95 μ and 4.4 μ (using the two flames and shutters as already described) before removing the specimen, and the results were found in excellent agreement. Throughout the work the various specimens were kept covered to prevent the deposition of dust.

The source of radiation usually remained constant to 1 part in 200 for several hours.

4. Regions of the Spectrum Examined.—The reflecting power of various substances was found for the following regions of the spectrum:

1. That part of the radiation of an acetylene (cylindrical) flame which is transmitted through a 1 per cent solution of cupric chloride[14] 2.5 cm in thickness. Such a solution is opaque to all radiations lying beyond 0.7 μ. The energy curve of this transmitted radiation does not differ markedly from the solar energy curve. The maximum of the transmitted energy lies at 0.6 μ.

2. That part of the radiation from an acetylene flame which is transmitted by a 1 per cent solution of cupric chloride 2.5 cm in thickness and a plate of green glass 2.5 mm in thickness. The transmitted radiation is fairly monochromatic, the maximum being at 0.54 μ.

3. The radiation of an acetylene flame which is transmitted through a 2 cm layer of water. The water cell transmits uniformly all the visible and part of the infra-red to 1.4 μ. The maximum of the energy curve of the transmitted radiation lies at 0.95 μ. By using a plate of red glass 2 mm in thickness, as indicated in the tabulated data, the radiations are more homogeneous, extending from 0.67 μ to 1.4 μ.

4. The radiation from a Bunsen flame which consists of a small emission band at 2.7 μ and a very strong band at 4.4 μ. About 90 per cent of the energy emitted by a Bunsen flame lies at 4.4 μ.

The purity of the maximum emission was tested with a thick plate of glass which is opaque to radiation lying beyond 3.5 μ. A sheet of plate glass 8 mm in thickness transmitted 5.8 per cent and a sheet 15 mm in thickness transmitted 3.7 per cent of the radiation from the flame. From this it appears that the homogeneity of the Bunsen flame radiation at 4.4 μ is not seriously affected by the weak radiations at 1.9, 2.7, and 5.3 μ.

5. The residual rays from quartz. The source of energy was the radiation from a Welsbach mantle which was reflected from two surfaces of quartz, which has two intense bands of selective reflection at 8.50 and 9.05 μ, respectively. The mean of the energy

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[14] This Bulletin, 7, p. 619, 1911, and 9, p. 110, 1912.

curve is at 8.8 μ. The maximum of this radiation was very homogeneous, only 0.43 per cent of the total radiation being transmitted by a glass plate 1.5 mm in thickness. The glass plate transmitted radiations to 4.5 μ, beyond which point, up to 8 μ, the reflecting power of quartz is extremely low, and throughout this region of the spectrum the radiation from the gas mantle is very weak.

6. The residual rays from fluorite. The source of energy was an incandescent gas mantle, the radiation from which was reflected from two plates of fluorite. The maximum of the energy curve was fairly homogeneous, 1.5 per cent being transmitted by glass (opaque beyond 4.5 μ) and 7.8 per cent being transmitted by a plate of fluorite 1.5 mm in thickness, which is opaque beyond 10 μ. The homogeneity could have been increased by adding another reflecting surface of fluorite, but it would have been at a sacrifice of the total energy available. Most of the black reflecting surfaces examined increase in reflecting power with wave length. Hence it is to be inferred that the observed values would be a trifle higher than here observed if the radiation had been more homogeneous. This is of minor importance, owing to the variation in reflecting power of the different samples of the same substances. The thermopile was covered with a plate of rock salt 0.8 mm in thickness, which is opaque to radiations beyond 30 μ; hence the maximum of the residual rays is shifted from its true position to about 24 μ.

5. Corrections to Observations.—A part of the energy reflected from the substance under examination escapes through the opening which admits the radiations into the mirror. The amount of energy thus lost was determined experimentally by covering temporarily a part of the silvered surface adjoining the opening by means of a thin sheet of aluminum blackened in an acetylene flame. The aluminum sheet was bent to fit the curvature of the mirror, and the area of the blackened surface was 10 by 20 mm. When not in use, this blackened surface was withdrawn through the opening in the hemisphere. The experiment consisted in noting the amount of energy (in galvanometer deflections) reflected from a layer of lead carbonate *with* and *without* the blackened surface in place within the hemisphere. The ratio of the galvanometer deflections in four complete series of observations varied from 97.1 to 97.5 per cent with a mean value of 97.3 per cent. On the assumption that, in the region occupied by the black surface, the illumination differs by a negligible amount from the value for the center of the mirror, the amount of energy lost by escaping through the opening is about 2.7 per cent of the total energy diffusely reflected within the hemisphere.

A further correction is necessary for the absorption of the diffuse radiations by the silvered surface of the hemispherical mirror. This correction, which depends upon the spectral region observed, was determined by placing a newly silvered plane mirror in the place occupied by the diffusing surface, *f*, Fig. 2, and at *c*, Fig. 1, *A*. This plane mirror was placed at the proper angle to reflect all the incident energy upon the interior of the hemispherical mirror and from thence upon the thermopile. The ratio of the galvanometer deflection for the energy reflected from the silvered surface to the deflection for the energy falling directly upon the thermopile gave the reflecting power of the two silver surfaces and the square root gave the value sought for a single reflecting surface. These values of the reflecting power, determined by this method, are in excellent agreement with the values obtained by the methods previously employed by other observers. The values of the reflecting power of silver, for the spectral regions employed, are given in Table I. In this same table are given the complete correction factors with which the observed (the "apparent") reflecting power of the various substances was multiplied in order to obtain the "true" (the absolute) values recorded in these tables. These factors are the reciprocals of the products obtained by multiplying the reflecting power of silver by the per cent of diffuse energy (97.3) which is intercepted by the hemispherical mirror. The silvered surface being well protected does not tarnish, so that these correction factors are constant for the investigation.

The corrections used by Royds, viz, (1) the correction for extra radiation falling upon the thermopile, as the result of scattering by air and dust particles when the incident radiation was projected upon the diffusing surface, and (2) the correction for reradiation upon the thermopile, as a result of warming of the diffusing surface by the incident radiation projected upon it, were nil in all cases except when very thick (0.3 to 0.4 mm) layers of lampblack were examined. The thick lampblack surfaces seemed to become heated when they appeared to radiate upon the thermopile. To the eye they were just as black as thin deposits of (acetylene) soot. Nevertheless, they apparently reflected from 2.5 to 2.8 per cent at 0.95 μ and 4.4 μ, and 8 to 12 per cent at 8.8 μ. A thin deposit of soot which appeared equally black and examined at the same time would reflect less than 1 per cent. The lampblack paints also reflected about 3 per cent, and they appeared very much lighter (reflected more of the incident radiation upon the thermopile, as could be observed visually) than the soot deposits. To prevent radiations of the heated thick films of soot from falling upon the thermopile, a thin (0.09 mm) sheet of glass was placed over, and about 1 mm from the surface of, the deposit of soot. The reflecting power of the thick layer at 0.95 μ was then reduced from 2.7 per cent to 1.08 per cent, which is about as low a value as was observed on a thinner film in which the conductivity to the brass block was effective. It was evident that the high values found for the reflection were caused by reradiation, and no attempt was made to examine very thick films, such as used by Royds. The thickness of the deposits of soot were of the order of 0.1 mm, which was found by experiment sufficient to absorb the maximum amount of radiation. The presence of stray radiations was also tested. For this purpose the reflecting surface (brass block) was removed from the carrier, *d*, Fig. 1, and the radiations coming through the opening, *h*, in the hemispherical mirror were permitted to pass out through *c* to the rear of the apparatus and fall upon a piece of black velvet. This test was applied at various times in the different spectral regions used and at various galvanometer sensitivities, but no deflection (as large as 0.1 mm) could be observed which was caused by radiations scattered by air and dust particles. The galvanometer could be read to 0.1 mm. The smallest deflections observed by reflection from the blackest surfaces were from 8 to 10 mm, and usually they were much larger. Hence, if there had been corrections such as observed by Royds, they could not have escaped notice. As mentioned elsewhere, the apparatus was designed so as to require a low radiation sensitivity, which eliminated these corrections, and the accuracy which one could easily attain was 1 part in 200 to 400. Evidently from the nature of the material it would have been illusory to attempt a higher accuracy. As an illustration of the accuracy attainable on a low reflecting power substance, the values found for platinum black (No. 16, Table II) may be cited. Two determinations on different days gave, respectively, 2.71 and 2.75 per cent for the reflecting power.

IV. REFLECTING POWER OF LAMPBLACK

The experimental results obtained in this research may be briefly portrayed by means of tabulated data and by brief comments relating thereto. As found by others, all sorts of lampblack (soot) surfaces can be prepared, differing in reflecting power, for the same flame and for different flames. The most permanent coatings are of course layers of paint made by mixing lampblack with turpentine, or, if the latter dries too slowly, with turpentine and alcohol. A weak alcoholic solution of shellac gives a much more grayish appearance to lampblack, as shown by the highest values obtained in Table I. But the reflecting power of the paint is so high that it is a question whether it might not be better practice to resmoke radiometers when the soot comes off.

Owing to the fact that many of the soot deposits became soiled before they could be examined in another spectral region, and also to the fact that in any given spectral region various deposits of soot were examined when they were removed from the brass blocks to be replaced by others, but few of the same deposits were examined in more than two or three parts of the spectrum. Hence (for clearness) Table I differs from the other tables in that the observations of reflecting power upon the same film in different spectral regions are joined by dotted lines. The additional observations in any spectral region, e. g., sperm candle, at 8.8 μ, are recorded without any special reference to the other observations.

Various experiments were performed on lampblack paints prepared from commercial lampblack. The best (purest) material gave reflecting powers varying from 2.9 to 3.1 per cent at 0.60 μ. This is in agreement with results obtained by depositing soot from burning camphor in a "watch crystal" and working it into a smooth paint with turpentine. As shown in Table I the reflecting power of lampblack paint is fairly uniform in the region of 4 to 8 μ, and a fair correction factor for (diffuse) reflection from a radiometer is from 3.3 to 3.5 per cent.

Finely ground boneblack, although having a very brownish color, becomes quite black (*R* about 1.5 per cent) when the turpentine has not thoroughly dried. From this it would appear that if the proper vehicle could be found it might be a much darker paint than ordinary matte lampblack paint.

The deposits of soot from the different flames were "hot" when the brass block was drawn through the flame or "cold" when the flame was cooled by a sheet-iron funnel with an opening 1 by 10 mm at the top through which the smoke issued and over which the brass block was held. The cold deposits usually had a higher reflecting power than the hot deposits. As already mentioned, layers 0.05 to 0.1 mm in thickness usually produced a maximum absorption. Thicker films gave higher "apparent" reflecting powers; but this was owing to heating of the surface, as the result of lack of conduction to the brass block, which then radiated upon the thermopile.

Some of the samples of soot appeared to have a slightly higher reflecting power in the visible than in the infra-red, as was shown by repeated measurements upon the same film. In the case of the deposit of soot (from a sperm candle) upon the layer of platinum black, No. 19, Table II, the reflecting power is considerably higher at 0.95 μ than at 4.4 μ. Whether this is due to the structure of the material, depth of penetration (which is a function of the wave length), and consequent variation in conductivity, is unknown. It does not appear unreasonable to suppose that for visible radiations which do not penetrate deeply the surface might become hotter (hence reradiation to the thermopile) than it would for the same amount of energy of wave lengths at 4.4 μ, which penetrates more deeply into the layer of soot, hence is absorbed nearer the brass surface, where conditions are more favorable for heat conductivity. It so happened that for the spectral regions of 0.95 μ, 4.4 μ, and 8.8 μ the incident radiation was of practically the same intensity.

In all cases the blackest obtainable deposits of any given source were investigated. The paraffin candle was discarded because of the difference in the boiling points of its constituents. The deposits were usually whitish. The rosin was burned in a sperm candle and it, as well as camphor (which burns without the presence of other ingredients), tends to give granular brownish deposits having a reflecting power of about 1.3 per cent in the visible spectrum. The cold deposits from a standard candle are fairly uniform, reflecting about 1.25 per cent. The "hot" deposits are much blacker and reflect about 1 per cent. Viewed at grazing emergence the surfaces appear as smooth as polished mirrors.

The blackest obtainable "hot" deposits were made in the acetylene flame, the lowest observed reflecting power being 0.42 per cent and the average deposit reflecting power being about 0.6 per cent at 0.6 μ. The "cold" deposits, obtained by holding a piece of sheet iron against the flame and allowing the resultant smoke to deposit upon the brass block, give somewhat higher reflecting powers, which are of the order of 0.8 per cent. None of these deposits have the brownish appearance to be observed in all deposits of soot from burning camphor. All these deposits were obtained by using standard burners. To test the effect of combustion without air being mixed with the gas before ignition, a glass tube was drawn down to a point which then formed the "burner." The flame emits, of course, a dense cloud of smoke. The deposit upon the brass block was smooth and brownish in color, similar to camphor soot. The reflecting power (see Table I, Acetylene, "no air") was 1.33 per cent, which is the average value of camphor soot.

In a previous paper[15] which gives data on the absorptivity of an acetylene flame attention was called to the peculiar selective absorption band in the visible spectrum which was similar to bands found in metals—e. g., nickel and platinum—which are in a colloidal state. Moreover, in the beginning of this paper attention was called to the seemingly colloidal properties of platinum black. Platinum black and acetylene soot are the blackest substances yet recorded, and of these the acetylene soot has the greater absorption. It is not unreasonable to consider the carbon particles (and the platinum in the electrolyte) to be in the colloidal condition at the instant of disruption of the gas molecule. In the hottest part of the flame one obtains the finest particles—i. e., the blackest surfaces. These surfaces viewed at grazing emergence appear as perfect mirrors having a high reflecting power.

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[15] This Bulletin, 7, p. 243; 1911.

Acetylene soot has a very low heat conductivity, which permitted warming of the superficial layers of a thick deposit of soot. The temperature rise was sufficient to cause reradiation upon the thermopile, and, as explained elsewhere in this paper, the apparent reflecting powers at 4.4 to 24 μ were of the order of 2.6 to 3 per cent, when an equally black, thin film reflected less than 1 per cent. By placing a thin sheet of glass in front of the thick film (this was possible for the region of 0.95 μ without disturbing the adjustments), which absorbed all the radiations of long wave lengths, the reflecting power was reduced from 2.6 per cent to 1.08 per cent, showing that the high value was erroneous. In practice a radiation instrument should therefore be covered with a film of acetylene soot which is less than 0.15 mm thick.

The blackest deposits of soot are obtained by holding the metal plate in the flame. But this will be rarely possible with radiation instruments. Furthermore, unless one constructs a special burner it is not possible to blacken large surfaces in the flame without having them streaked with grayish colored material. One must therefore use cold deposits and standard material. The standard sperm candle is the most promising source, the reflecting power of the blackest surfaces being about 1 per cent in the visible spectrum, which is the order of accuracy of radiation work at the present day. It is difficult to remove fine dust from these surfaces; hence it appears advisable to use a hemispherical mirror to intercept the diffusely reflected rays.

For the absorbing surface of a secondary radiometer which has been calibrated against a primary standard it seems desirable to use the best quality of lampblack paint, the vehicle being a volatile turpentine. If the turpentine has polymerized and dries slowly, then a mixture of turpentine and alcohol should be employed. The turpentine is of course used simply to render the lampblack adhesive, and it is used instead of the dilute alcoholic solution of shellac because, as already mentioned, the latter tends to produce a grayish surface. All these surfaces are of course perfectly matte. The lampblack paint is easily freed from dust, hence is to be preferred to soot when the instrument must be operated in the open air.

V. REFLECTING POWER OF PLATINUM BLACK

The electrolytic deposits of platinum black were deposited upon sheet platinum 0.02 mm in thickness and having an area of about 0.5 by 5 cm. These platinum sheets were then mounted upon the brass blocks already described by means of Khotinsky cement. The first surfaces were made from a solution of platinum chloride, which usually gave grayish deposits. After many attempts which included Nos. 4 and 5, Table II, a new solution of chloroplatinic acid was prepared by dissolving a known weight of platinum (4 g of sheet platinum) in aqua regia. This material was evaporated to as near dryness as was possible over a water bath. This evaporation process was repeated after adding hydrochloric acid. The resulting material, which is a thick reddish sirup, contained 8.3 g (theoretical value) of H_2PtCl_6. From this a solution of the proper concentration recommended by Kurlbaum[16] was made up, viz, 5 g of $H_2Pt\ Cl_6$, 150 g of water, and 0.04 g of lead acetate. The deposits of platinum black were made by passing a current of 0.03 ampere per cm^2 of exposed surface, the time being varied from one to seven minutes. By occasionally jarring the electrodes the escape of gas bubbles was prevented. This procedure seemed to assist in forming black deposits. The cathode (strip to be blackened) was, of course, placed between two strips of platinum, which formed the anode. The distance between the anode and cathode was about 2 cm. The platinum strips were made sufficiently long and every other precaution was taken so as not to contaminate the solution by contact with the copper leads.

The manner in which the reflecting power decreases with increase in thickness of the deposit is well illustrated in the samples, Nos. 14 to 20, given in Table II. The reflecting power is a function of the wave length, a much thinner deposit being required to produce a maximum absorption for the spectral region of 4.4 μ than for the region of 8.8 μ. At normal incidence the thin deposits appear darker and more velvety than the thick ones, but a slight deviation from the normal increases the reflecting power, as illustrated in No. 4 at 8.8 μ. Moreover, some of the very dark velvety thick deposits tend to give high values beyond 4.4 μ, although they show an abnormally low reflection in the visible spectrum. This was definitely determined by repeated tests on No. 16, which was similar in appearance to No. 17. To the eye No. 16 appeared slightly darker than No. 12. The deposits Nos. 18 and 19 were on the opposite sides of a strip of platinum, deposited at the same time. The reflecting powers (1.78 and 2.13 per cent, respectively) are considerably different at 8.8 μ. Of course this is quite a severe test of reproducibility. Deposits that were continued for more than seven minutes became rough and nodular. From Table II it may be noticed that the deposition of platinum black should be continued for at least five minutes to obtain a maximum absorption at 4.4 μ; and the best practice is to continue the process six to seven minutes, when the maximum absorption is attained at 8.8 to 24 μ. The reflecting power then rises gradually from about 1 per cent in the visible to 3 per cent at 24 μ.

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[16] Kurlbaum: Ann. der Phys. (3), 67, p. 846; 1899.

The deposits are quite adhesive, so that if kept free from dust the reflecting power changes but little with age. This is illustrated in the two series of measurements on Nos. 18 and 20 at 4.4 μ, which were reexamined after an interval of about a month, when the apparatus was entirely readjusted and different-sized slit images were used. The ever-present particles of lint were first removed by blowing gently with the breath. In the second set of measurements on Nos. 18, 19, and 20 the observations at 0.95 μ and 4.4 μ were made in succession before removing the specimen. It is, of course, to be understood that owing to the labor involved in making the adjustments of the quartz and fluorite plates the regions of 8.8 μ and 24 μ were examined separately. Hence, the specimens were all examined in succession at 8.8 μ before turning to the region of 24 μ.

The deposit No. 19 was smoked with soot from a sperm candle, which raised the reflecting power in the visible spectrum without materially affecting the region of 4.4 μ.

Chemically precipitated platinum black was also examined. It is quite brownish in appearance. One of the three samples was a layer of the material pressed upon the brass block, as already described. The others were painted on the brass plates by means of a solution of alcohol and turpentine, which dries quicker than turpentine. In both cases the reflecting power is high (2 per cent) in the visible, increasing to 12 per cent at 24 μ. This is owing to the property of the material and not to the thickness of the layer. The thickness of the layer in the various samples examined varied from 0.1 to 0.3 mm. By mixing lampblack and platinum black, equal parts (by bulk), and applying it as paint the reflecting power is raised in the visible and reduced at 24 μ. This specimen was then covered with soot and the reflecting power was reduced to about 1.4 per cent. Although the reflecting power is now more uniform throughout the spectrum, it is not more so than the electrolytic deposit, which reflects only about one-third as much energy. Hence the precipitated material or mixtures of the same are less desirable than the best obtainable lampblack paints. (See Table I.)

With lampblack difficulty was experienced in making measurements owing to reradiation, which resulted from the low heat conductivity and consequent heating of the thick layers of soot. This was not experienced in platinum black owing to better thermal conductivity. The glass window over the thermopile absorbed this reradiated energy from the black surfaces. In the case of platinum black (which was more thoroughly studied than soot because it gives more permanent surfaces) the reflecting power at 0.95 μ was determined with a glass and with a rock salt window on the thermopile. The values are in perfect agreement, showing that there was no reradiation upon the thermopile when the rock salt window was used. The values are therefore to be considered reliable, and the slight variations in the reflecting power observed in the table are owing to differences in the structure of the deposits. Even with the new solution one of the deposits came out quite grayish in appearance. This seemed to have been caused by excessive agitation of the electrolyte to keep the electrodes free from the stream of gas bubbles.

An examination of 6 surface bolometers (12 branches or 24 surfaces), purchased from instrument makers, showed that all the herein-described deposits of platinum in which the deposition of platinum black was continued for at least 4 minutes, were better than the surface of the best of these bolometers. The bolometer surfaces (even the thick deposits) showed bright spots where the metal was exposed. One bolometer had a thin deposit, similar to the 1 to 2 minute deposits shown in Nos. 13 and 14, Table II. From this the conclusion is to be drawn that the correction for diffuse reflection from a commercial surface bolometer is from 2.5 to 3 per cent or perhaps as high as 5 per cent. In fact, with the improved facilities now at hand, it is better to obtain new data on the total radiation of black bodies rather than attempt to correct the old data, which are now of historical interest.

With this end in view, now that the present research is completed, it is purposed to use the knowledge gained as well as the hemispherical mirror and thermopile in obtaining data on the constants which enter into the Stefan law of total radiation.

VI. REFLECTING POWER OF GREEN LEAVES

The first examination of diffuse reflecting power of growing leaves was undertaken in May, 1908, the apparatus employed being a bolometer, a mirror spectrometer, and a fluorite prism. The leaves were mounted upon a holder beside a silver comparison mirror, and the observations were carried out in the same manner as was employed in the determination of the reflecting power of plane mirrors.[17] The angle of incidence was 45°, and the distance of the reflecting surface to the spectrometer slit was about 6 cm. The source of light was a Nernst glower. The values thus obtained are of course only relative for the different wave lengths. The observations extended to 3μ (see Fig. 3), and in all cases there appeared to be a decrease in the amount of energy reflected with increase in wave length. This seems plausible, for the increase in opacity with wave length beyond

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[17] This Bulletin, 2, p. 457, 1906, and 7, p. 197, 1911.

1.4 μ, which obtains in water, would decrease the amount of radiation that can return by internal reflection. The curve "Red Oak, II a," was obtained after the sample "Red Oak, II," had remained upon the spectrometer overnight, when considerable of the moisture had evaporated. It is therefore to be expected that the reflecting power would be less than when the cells contained moisture.

For magnesium carbonate the decrease in reflecting power with increase in wave length might result from a decrease in refractive index, which obtains in all similar "transparent media." This decrease in reflecting power is more noticeable in the region of 4.4 μ.

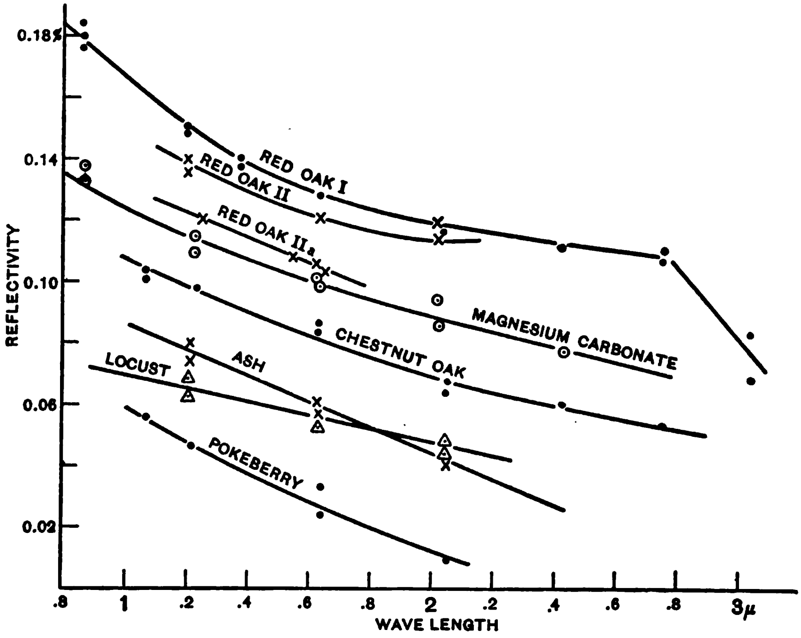

Fig. 3.—*Reflecting power of green leaves*

In this year's work, unless otherwise noted, the green leaves were examined in the latter part of May. The oldest (darkest green) leaves were selected, which were entirely free from injury. The reflecting power is somewhat less for the fully matured leaves of the oak and the tulip tree, Table III, gathered in July. The clover, locust, laurel, and lilac leaves appeared well matured when examined.

From Table III it appears that vegetation reflects about 25 per cent of the solar rays. The value may be a little higher than this, for the absorption cell used with the acetylene flame produces an energy distribution, which is somewhat richer in red and infra-red rays than obtains in average sunlight. This value can not greatly differ from the true one, however, for using monochromatic radiation corresponding closely with the color of leaves (green glass; $\lambda = 0.54\mu$), the observed reflecting power of clover, lilac, and tulip tree leaves is not much higher than for the composite rays which have a maximum at 0.60 μ. These tests were of course applied on the same leaf by simply placing a green glass before the absorption cell. The mullein leaf gave surprising results, the reflecting power differing but little from that of other leaves. Because of the densely wooly surface the expectation was to observe a high reflecting power. Evidently the tomentous covering contributes but little in raising the reflecting power. This is of interest in connection with desert plants having a wooly covering. The transmission was difficult to observe owing to the warming of, and the consequent reradiation from, the leaves upon the thermopile. The leaf to be examined was placed over the thermopile, the distance between the two being about 1 mm to avoid heat conductivity to the thermopile. The transmission of a leaf (after correction for reflection) is about 20 per cent, Table III. The two kinds of leaves, lilac and locust, differed considerably in thickness.

According to the measurements of Brown and Escombe [18] the absorption of leaves is 68 to 69 per cent of the total solar energy. Their values for the loss of solar radiation by transmission through the leaf are of the order of 30 per cent, depending, of course, upon the kind of leaf. These values are in fair agreement with present observations, considering the nature of the material and the apparatus used. Brown and Escombe (loc. cit.) have also published values for the total energy expended in internal work, viz, the energy used for photosynthesis (about 1.5 per cent) and the energy used in transpiration of water (10 to 60 per cent, depending upon the kind of leaf). They found that the maximum temperature excess above its surroundings to which a growing leaf can be raised in still air and exposed to the sun is about 0°.02.

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[18] Brown and Escombe: Proc. Roy. Soc., Lond., B, 76, p. 29; 1905.

All these data are very instructive when compared with the reflecting power of building material, e. g., brick, marble, granolith, and asphalt, given in Table V. In the latter the energy absorbed is not utilized in internal work, and the temperature may rise a very considerable amount, the rise depending upon exposure to wind, etc. Hence in marked contrast with vegetation, when the sun is obscured or has set, the building material continues to reradiate the energy absorbed during the daytime.

It is beyond the scope of this paper to discuss the economic importance which would result from the application of these data. Suffice it to say that until traffic demands the full width, a considerable portion of the total width of a street and sidewalk should be occupied by trees and grass instead of asphaltum and granolith. The same thing is true of observatories, which should be surrounded with thickly growing vegetation, such as Norway pine and dwarf evergreens. Evergreen trees which are not too tall to interfere with telescopic work should stand thick and close to an observatory, so as to shield it from the sun.

The reflecting power of a green leaf in different spectral regions is given in Table V. The reflecting power is much higher for an old leaf from which the chlorophyll has disappeared. A bright yellow undried leaf of the tulip tree reflects almost half of the incident light, Table III.

VII. REFLECTING POWER OF PIGMENTS

The powdered material was mounted upon the brass block, Fig. 1, *D*. In some cases the material was moistened with water containing a trace of gum arabic, but there was difficulty in causing the material to adhere to the block. This difficulty was overcome by putting a thin coat of shellac varnish upon the brass block. After the shellac had become quite dry a thick (0.3 mm) layer of the powder was pressed upon the block and flattened with a plate of glass. The effect of smoothness usually was not noticeable. However, in substances having high metallic reflection, e. g., silicates, carbonates, and sulphates, at 8 to 9 μ (see Table IV, quartz at 8.8 μ) the smoothness of the surface was of importance. For example, a rather coarse-grained sample of powdered feldspar reflected 10.3 per cent at 8.8 μ. On pressing the material into a more compact mass the reflecting power rose to 14.6 per cent.

Zirconium oxide mounted by the two methods gave concordant results. Owing to the high reflecting power of the material so much energy was thrown upon the thermopile that the glass window, which absorbs about 15 per cent of the radiations at 4.4 μ, became sufficiently warm to cause the galvanometer to drift. It was therefore impossible to obtain trustworthy values of the reflecting power of the white powders with the glass window in place. It was therefore replaced by a window of rock salt. When examining the black substances at 4.4 μ the opposite condition obtained. In comparison to the total amount reflected the temperature rise was such that reradiation from the lampblack became appreciable. The glass window was therefore used over the thermopile to absorb the radiations from the black substances.

As mentioned elsewhere, there is a distinction between the high reflecting power observed at 4.4 μ and at 8.8 μ. The high values (40 to 50 per cent) at 4.4 μ are to be ascribed to internal reflection. On the other hand, it is a common property of insulators to be very opaque beyond 5 μ and to have bands of selective reflection beyond 6 μ. For example, carbonates have bands of selective reflection in the region of 6.9 μ; sulphates and silicates have bands of strong selective reflection in the region of 9 μ. Hence the high reflecting powers observed in the case of carbonates and silicates, Table IV, at 8.8 μ is owing to selective reflection from the surface of the particles.

The low reflecting power of the aluminum oxide at 8.8 μ is of interest, because the observations were made in the region of anomalous dispersion, where the reflecting power is abnormally low,[19] followed by bands of metallic reflection at 12 to 14 μ. Zinc oxide also has a low reflection at 8.8 μ. The reflecting power of a plane highly polished surface is low and uniform throughout this region.[20] By pressing the powdered material into a smooth, compact mass the reflecting power (3.2 per cent) was not materially increased. This shows that it is not a surface phenomenon, as found in silicates and carbonates. For example, in lead carbonate which was pressed into a smooth, hard mass comparable with that of the zinc-oxide sample just mentioned the diffuse reflecting power was raised from 8.3 to 13.2 per cent. These surfaces, including zirconium oxide, which has a low reflecting power, appeared dull at normal incidence, but when viewed at grazing incidence appeared like highly polished mirrors. The difference between "surface color" and "body color" is well illustrated in lead carbonate and in zinc oxide.

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[19] See Investigations of Infra-red Spectra, Publication No. 97, p. 18, Carnegie Institution, 1908.

[20] Carnegie Publication, No. 97, p. 17.

Lead oxide appears to have an extremely high reflecting power in the region of 8.8 μ, and by using a plane highly polished surface the reflection spectrum of this substance should be examined for residual rays in the region of 8 to 10 μ.

Many of the substances examined show a high reflecting power for the spectral region of 24 μ, from which it is to be inferred that they possess strong selective reflection in this region of the spectrum. It is of course already known that carbonates and silicates have bands of selective reflection in this region of the spectrum.

Mention was made in the beginning of this paper that the most efficient paint to protect a building from solar rays is one having a high reflecting power in the visible spectrum and a low reflecting power in the region of 8 to 9 μ. Of the various materials used in paints, zinc oxide would be the most efficient radiator in the region of 8 to 10 μ, but, as will be noticed presently, it does not appear to reflect so highly as lead carbonate in the visible and in the violet. The same condition is found in the dry pigments. However, the white lead does not appear so bluish white as the zinc oxide.

VIII. REFLECTING POWER OF MISCELLANEOUS SUBSTANCES

In Table V are given the data obtained on various substances not closely related to the groups already described. The ground and the cleavage surface of white marble illustrate the effect of grain size upon the reflecting power as mentioned in the beginning of the paper. The brown sand examined illustrates the average reflection from material obtainable along roadsides. Fine dust would probably have a higher reflection. The effect of fine dust upon asphaltum is also shown in this table. The sample examined was a piece of road material which was being removed after some years usage. The granolith was a piece of pavement which was washed free from dust. Of the other building materials the slate used in roofing is of interest, for it reflects only about 6.7 per cent of the solar rays.

For convenience in tabulating, the data on "bluestone" (the dark-colored sandstone extensively used in buildings) are given in Table IV. This material cleaves into thin flat lamina. The reflecting power at 8.8 μ and 24 μ is very high, owing to the bands of selective reflection (silica) and the presence of fine crystal surfaces. The reflecting power of powdered feldspar and of quartz ("French flint") are also given in Table IV. These data are of interest in connection with the question whether the observed lunar radiation in the region of 8 to 10 μ is really, to a large extent, selectively reflected solar radiation.[21]

Black velvet has a very low reflecting power. The reflecting power of the sample of black felt recorded in Table V was examined several times on different days. The final test was made with a thin sheet of glass over the felt in addition to the glass window covering the thermopile, and in another test the thermopile was covered with a sheet of red glass 2 mm in thickness. The values for the reflecting power were always high, and it was concluded that this is owing to the manner in which the dye has affected the cellular structure of the fibers. Other samples of woolen cloth were examined, all of which had a high reflecting power. (See Table VI.) A similarly high reflecting power was also observed in all of the cotton cloths examined except the "sulphur black," which reflected only about 2.43 per cent. Using two thicknesses of this cloth the reflecting power was 2.37 per cent. This shows that the high reflection in the equally thick woolen samples was not caused by warming and reradiation. Similarly, the high reflecting power (33 per cent) of one and of two layers of "Diamine fast black," Table VI, showed that this was not owing to reflection from the brass block upon which the cloth was mounted. These samples of cloth were attached to the brass blocks already described by means of a thin coat of shellac varnish, which was allowed to become quite dry before applying the cloth. The samples of cloth recorded in Table VI were taken from the pattern sheets published in the Journal of the Society of Dyers and Colorists for 1912.

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[21] Coblentz: Phys. Rev. 24, p. 307; 1907.

At first it was thought that the high reflection might be caused by the superposition of an infra-red fluorescent radiation (of wave lengths between 1.5 μ and 3 μ) upon the diffusely reflected radiations of $\lambda = 0.6$ μ and 0.95 μ, respectively; but the tests applied did not give conclusive evidence of such a phenomenon. This is a question that requires further investigation.[22]

IX. SELECTIVE REFLECTION AND EMISSION OF WHITE PAINTS

The problem is to find a white paint that reflects a maximum amount of visible rays and a minimum amount of infra-red rays of wave lengths between 6 and 10 μ. In this manner a large portion of the solar rays will be reflected into space, and the rise in temperature resulting from the solar rays that are absorbed will be prevented by reradiation, which is facilitated by a high emissivity (low reflection) at 6 to 10 μ.

Unfortunately, the paint (zinc oxide) that fulfills the latter condition has a lower reflecting power than white lead in the visible spectrum. It can not be used for exterior work. The next best primary paint for exterior work is white lead, but like all carbonates its infra-red emissivity is not as high as that of zinc oxide. Radiometrically it would therefore appear to be better to use a mixture composed of white lead and as high a proportion of zinc oxide as is permissible to form a good paint.

The carbonates, sulphates, and silicates have bands of strong metallic reflection in the region of 7 to 9 μ, which suppress the reradiation of the absorbed solar rays. In binary mixtures, sulphates and silicates are less desirable than carbonates, for their infra-red reflecting power is higher and the bands do not lie close to those of lead carbonate. This suppresses the emissivity over a wide range of the infra-red spectrum. Of course, a few (5 to 8) per cent of silica or china clay, which is said to improve white lead mechanically, can not seriously affect the radiating properties of the primary, viz, white lead. The combination of calcium sulphate and of barytes with white lead appeared much darker than a similar combination with calcium carbonate.

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[22] As this paper goes to press some results on diffuse reflection have been published by Dr. Nutting. (Trans. Illum. Eng. 7, p. 412; 1912.) The instrument used by him for measuring the diffuse reflection is built upon an entirely different principle. Nevertheless, our results are entirely in agreement. For example, he found the reflecting power of black velvet to be 1.8 per cent (really 1.75 for the mean of the two positions of his photometer), as compared with 1.75 per cent by the present method. For one sheet of ordinary white paper he found a reflecting power of 72.2 per cent and for several superposed sheets he found a value of 73.3 per cent. In the present research the reflecting power of a single sheet, of the same kind of paper as used by him, was found to be 71.7 per cent and for two superposed sheets it was 73.4 per cent.

The white paints examined quantitatively for reflection were samples which had been ground in linseed oil under standard conditions.[23] They were painted (five or more coats) upon the aforementioned brass blocks and were thoroughly dry. There was no marked difference in the reflecting power of white lead made by different processes (American, Dutch, and French), the reflecting power of various samples varying from 74.3 to 76.0 per cent. (See Table VI.) Similarly, the samples of zinc oxide paints reflected from 68 to 69 per cent. This agrees with previous observations on the dry pigments, which show that lead carbonate has a higher reflecting power than zinc oxide. A mixture of equal parts of white lead and of zinc oxide reflected 71 per cent. In view of the fact that the reflecting power of aluminum, Table I, is high in the visible and in the ultra-violet, it was of interest to determine whether sheet aluminum would be more satisfactory than white paint for protecting a building against warming by solar rays. The difference in reflecting power of aluminum and white paint is not so marked in the visible spectrum as in the infra-red Both materials absorb considerable sunlight, but the aluminum has the lower emissivity for the radiations at 6 to 12 μ. Hence, it can not radiate the absorbed energy as rapidly as the white paint and its temperature rises above that of white paint. This conclusion is borne out by the following experiments, in which the temperature of two similar plates of aluminum was observed before and after one plate was painted with white lead ground in pure linseed oil. Two sizes of sheet aluminum were tested: A, 46 by 48 by 0.718 mm; B, 68 by 69 by 0.245 mm. Thermocouples of copper and constantan wires were inserted and riveted in holes drilled through the aluminum plates, and as a further attempt to obtain good contact the junctions were tightened with Wood's alloy. The constantan wire was 0.31 mm and the copper was 0.40 mm in diameter. The cold junctions were kept in ice. The aluminum sheets were mounted side by side upon a board of yellow poplar 20 by 19 by 1.8 cm and exposed to direct sunlight. The temperature of the pairs of sheets, A and B, and the difference in temperature was measured by means of a potentiometer. The thick unpainted plates (A), covered with window glass and exposed to sunlight, showed no difference (difference = 0°.05) in temperature; but in the thin sheets B–I was about 1°.1 hotter than B–II, when at a temperature of about 37° C. The tests were made on a somewhat windy day, which prevented accurate measurements without glass covers over the aluminum plates. There is no reason, however, for thinking that the observations would have been different without the glass. Sheets No. II of both A and B were then given two coats of pure white-lead paint. Exposed to sunlight under glass the temperature of the painted surface of A (II) was about 0°.8 higher than A–I. Similarly, the temperature of B–II (the painted surface) was about 0°.9 higher than B–I, the actual temperature being from 46 to 47° C. The sky was perfectly clear (Oct. 7, 1912) with only a slight breeze blowing. Without the glass coverings, which is the test of most interest, the unpainted aluminum plate was the hotter. For A–I the temperature of the bare aluminum was 3°.0 to 3°.1 higher than the exactly similar sheet having two coats of white-lead paint. The actual temperature of A–I was about 44°.7. Similarly, for B–I the temperature excess of the bare aluminum sheet was 2°.3 to 2°.4, the actual temperature being about 43°.7. The intensity of the solar radiation, Q, was about 1.161 g cal. cm^2 min.

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[23] Proc. Amer. Soc. for Testing Materials, 11, p. 226; 1911.

These tests were repeated, using three coats of paint. The weather was perfectly clear (Oct. 10, 1912), and no breeze blowing. The intensity of the solar radiation was 1.157 gr. cal. cm^2 min. The plates were exposed directly to the sun—i. e., no glass intervening. For A–I the temperature excess was 4°.1 to 4°.3, the actual temperature being about 45° C. Similarly, for B–I (unpainted aluminum) the temperature excess was 3°.0 to 3°.2, the actual temperature being about 42°.7. From these tests it is evident that a metal roof painted with several coats of white paint is far superior to one of bright metal. As already mentioned, this is owing to the fact that white paint has a higher emissivity than metals in the infra-red.

The unpainted sheets of aluminum (A–I, B–I) were then given three coats of zinc oxide paint. When thoroughly dry, the sheets containing the zinc oxide paint appeared to be at about the same (+0°.1) temperature as obtained in the white lead. Another coat of paint was then applied (making four coats in all) to each sheet. When exposed directly to solar radiation, the temperature excess of the zinc oxide paint for the thin sheets, B, was ±0°.1 and for the thick sheets it was about +0°.5. From this it appears that, in comparison with white lead, what is gained in higher emissivity in the infra-red in the zinc oxide paint is lost by its higher absorption (lower reflecting power) in the visible spectrum, so that radiometrically it is no more efficient than white lead.

The white lead paint was removed from the sheets, A–II, B–II, which were then painted with a matte layer of the lampblack, used in the experiments already described. When exposed directly to the sun, the temperature of the lampblack sheet, A–II, was about 16° higher than the zinc oxide paint, A–I, the actual temperature of the lampblack being about 52°.2 for solar radiation of intensity, Q = 1.16. Similarly, the temperature of the lampblack sheet, B–II, was 17°.5 higher than the zinc oxide plate, B–I, the actual temperature of the aluminum sheet covered with lampblack paint being about 53°.3 C and the room temperature (i. e., in the shade) being about 23°.1 C. The infra-red reflecting at 8.8μ differs but little for these two substances; hence there is no great difference in their emissivities for low temperatures. In the visible spectrum the absorptivity of the zinc oxide is only about 30 per cent, and for lampblack it is 97 per cent. Hence the lampblack must become the hotter, for it absorbs energy at three times the rate and it emits energy (low temperature radiation) at practically the same rate as does the zinc oxide paint.

X. SUMMARY.

1. This paper gives an account of an investigation of the reflecting power of matte surfaces of various substances (also of polished surfaces of silver and aluminum) for the spectral regions of 0.54, 0.60, 0.95, 4.4, 8.8, and 24μ.

2. The diffusely reflected radiations were collected by means of a hemispherical mirror and projected upon a surface thermopile

of bismuth and silver, which was used to measure the intensity of the incident and the reflected radiations.

3. The substances examined include lampblack, platinum black, pigments, white paints, green leaves, dyed cloth, and building material. The object of the investigation was to find the blackest and the whitest substances—the former to be used as absorbing surfaces of radiometers, the latter to be used as a covering for buildings exposed to intense sunlight.

4. Methods are given for preparing standard black surfaces, and quantitative data are given for the loss by reflection of the same.

WASHINGTON, *October 31, 1912.*

NOTE I.—VARIATION OF THE SPECULAR REFLECTING POWER OF SILVER WITH ANGLE OF INCIDENCE

The variation of the specular reflecting power of polished metals with the angle of incidence, using unpolarized light, has been investigated by various observers.[24] The measurements were made photometrically and also radiometrically, and the general conclusion is that the reflecting power passes through a minimum, for angles of incidence between 60° and 70°, for unpolarized light. For silver no conclusive quantitative data, which is needed in spectroradiometric work, was available, and the question was therefore investigated anew.

In spectroradiometric work it is customary to have the collimating arms fixed and to rotate the prism table, upon which is mounted a plane reflecting mirror in addition to the prism. This combination forms the Wadsworth method [25] for maintaining a minimum deviation for all the rays. The angle of incidence of the light upon the mirror varies as the prism is rotated, and the problem was to determine the resultant change in reflecting power of the silver mirror. This is a difficult problem, for the variation in reflecting power is small, and it is necessary to keep the source of energy and the radiometer sensitivity constant for a considerable time. This question was therefore investigated only for the angles of incidence (about 54° for $\lambda = 0.5896\mu$; the angle between the mirror and the adjacent prism face is about 80°) at which the rays must fall upon the mirror in order to pass through a fluorite prism at minimum deviation. As used at present in determining spectral energy curves of a black body, this involves an increase of about 4° in the angle of incidence in passing from $\lambda = 0.5896\mu$ to $\lambda = 6\mu$.

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[24] Provostaye and Desains: (3), **30**, p. 276; 1850. Jamin: Ann. Chim. et Phys. (3), **19**, p. 296; 1846 Knoblauch: Ann. der Phys. (3), **1**, p. 1; 1887.

[25] Wadsworth: Phil. Mag. (5), **38**, p. 346; 1894.

For determining the variation in reflecting power a freshly silvered plane mirror was mounted upon the prism table of a small, high-intensity spectrometer having triple achromatic lenses 6 cm in diameter and 18 cm in focal length. The collimating and the telescope arms were attached to the spectrometer table by means of an automatic slide-arm arrangement, such as is commonly used in maintaining a prism at minimum deviation. The energy reflected from the mirror was measured by means of a bismuth-silver thermopile[26] of 20 junctions, 1.4 mm wide, which was mounted in place of the eyepiece of the movable telescope. The collimating arm, with a slit 1.2 mm wide, was fixed, and before it was placed a Nernst glower. Beween the glower and the slit was placed a shutter and a cell, 2 cm in thickness, containing a 3.5 per cent solution of cupric chloride, which absorbs all the infra-red beyond 0.7μ.[27] This limited the radiations to be measured to the region of the visible spectrum, with the maximum at about 0.55μ.

Owing to the fact that the spectrometer was not adapted to a large rotation of one arm, with the automatic slide arm in place for maintaining minimum deviation (really for varying the angle of incidence upon the mirror in this investigation), the variation in reflecting power was determined for an angle of incidence of 54° and for 64°. This required a rotation of 20° of the telescope arm, and although the whole was completely inclosed to exclude stray light there was an appreciable shift in the zero reading of the galvanometer in passing from one to the other of these two positions. This of course does not interfere with the observations when thermal equilibrium has been established after moving the thermopile to the new position. The various sources of error were of course tested before making measurements. The most important error that might be introduced would result from the automatic slide-arm arrangement, which might not always cause the slit image to fall exactly upon the thermopile when changing to a different angle of incidence. By experimentally determining the axis of rotation of the mirror and making all the rotations in the same direction to eliminate backlash this error was eliminated.

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[26] This Bulletin, 9, p. 7; 1912.

[27] This Bulletin, 7, p. 619; 1911; and p. 110, 1912.

The variation in reflecting power was determined by noting the galvanometer deflections when the angle of incidence was varied 10° (also 8°), the source of radiation being kept constant. In all six distinct series of measurements were made. With an increase of 10° in the angle of incidence the galvanometer deflections were decreased by amounts varying from 1.0 to 1.6 per cent, the mean value being 1.2 per cent. This gives a decrease of 0.12 per cent per degree increase in the angle of incidence for angles of incidence varying from 54° to 64°. From this it is evident that the correction to spectral energy curves owing to the difference in reflecting power for different angles of incidence is negligibly small. It would of course be profitable to determine this variation over a wider range, but much more elaborate apparatus would be required.

TABLE I

Reflecting Power of Lampblack

Wave length λ max.	0.54μ	0.60μ	0.95μ	0.95μ (Red glass)	4.4μ	8.8μ	24.μ	
Silver	93.2%	89.9%	93.4%	94.6%	98.0%	98.0%	98.5%	
Aluminum		68.5			92.3			
Correction factor	1.102	1.143	1.100	1.086	1.049	1.049	1.043	
Lampblack paint		2.94			3.24			
		3.02			3.29			
		3.58			3.60			Alcohol+shellac
		3.72			4.86			
		3.10	3.38	3.36	3.34	3.75	4.4	
Paraffin candle			0.97%					
(Cold soot)		1.07						
		1.43						
Rosin			1.26		1.31			
					0.85	1.07	2.8	

TABLE I—Continued

Reflecting Power of Lampblack—Continued

Wave length λ max.	0.54μ	0.60μ	0.95μ	0.95μ (Red glass)	4.4μ	8.8μ	24.μ
			0.91		0.67	1.44	3.9
			1.02		0.93	1.27	4.1
Sperm candle			1.25		1.03		
			1.07		0.77	1.28	
			1.01		1.36	1.23	
					1.28	0.87	
Camphor			1.34		1.38	1.46	
			1.30		0.95	1.65	5.7
			1.36		1.15		
(Paint)			2.80		3.24		
Acetylene			0.59				
			0.82		0.92	1.12	3.0
			0.64		0.71	1.24	
			0.54		0.81		
			0.42		0.71		
(Cold deposit)			0.86				
(No air)			1.33				

TABLE II

Reflecting Power of Platinum Black

Wave length λ max.	0.60μ	0.95μ	0.95μ (Red glass)	4.4μ	8.8μ	24μ
Chemically precipitated paint	2.01%	2.92		6.00		
		2.43	2.50			
			2.53	5.76	8.67	12.1
Platinum black and lampblack paint	2.77	2.70	2.84	4.02 3.94	6.44	8.2
Ibid. and soot	1.46	1.38				
Electrolytic No. —						
4		1.22		8.8	13.2	
5		0.98		2.64	4.63	
Ibid		1.16		2.68		
14; 1 min					25 to 30	
13; 2 min					11.3	
9; 3 min					5.9	
10; 3 min		0.99		1.72	3.66	7.5
11; 4 min				1.54	2.40	4.4

TABLE II—Continued

Reflecting Power of Platinum Black—Continued

Wave length λ max.	0.60μ	0.95μ	0.95μ (Red glass)	4.4μ	8.8μ	24μ
Electrolytic No. —						
Ibid		1.16		1.59		
12; 5 min		1.12		1.50	1.84	3.9
16; 5 min		0.85		1.48	2.71	
15; 6 min		1.01		1.51	2.23	3.4
18; 6 min				1.33	1.78	
Ibid		1.08		1.35		
19; 6 min					2.13	
19 and soot				0.93	1.27	4.1
Ibid		1.25		0.99		
17; 7 min		0.98		1.44	1.82	3.3
20; 7 min				1.29	1.88	2.9
Ibid		0.97		1.31		

TABLE III

Reflecting Power of Green Leaves

Wave length λ max	Remarks	0.54μ	0.60μ
Clover (*Trifolium pratense*)		23.9%	21.3%
Lilac (*Syringa vulgaris*)	May 3	26.0	25.3
	June 8		23.6
	Transmission		19.6
Locust (*Robina Pseudacacia*)	May 3		25.4
	June 8		23.9
	Transmission		20.7
Tulip tree (*Liriodendron tulipifera*)	May 3	28.1	27.2
(See also Table V)	July 29		22.0
	Oct. 31	47.0	48.8
Laurel (*Kalmia latifolia*)			23.2
	Rear side		27.7
Basswood (*Tilia Americana*)			26.9
Elm (*Ulnus Americana*)			25.7
Oak (*Quercus rubra*)	Young leaf		29.3
	Dark green		21.8
Mullein (*Verbascum thapsus*)			24.2

TABLE IV

Reflecting Power of Pigments

Wave length λ max.	0.54μ	0 60μ	0.95μ	0.95μ (Red glass)	4.4μ	8.8μ	24μ
Cobalt oxide, Co_2O_3	....	3.02%	3.92 4.04 2.49	....	13.9	14.6 11.8	5.9
Copper oxide, CuO	....	....	23.5	....	15.2	....	4.4
Chromium oxide, Cr_2O_3	24.1	27.0	44.6	....	32.9	5.0	8.2
Lead oxide, PbO	....	51.8	....	....	50.6	25.6	9.5
Red iron oxide, Fe_2O_3	....	26.3	41.0	53.6	29.9	3.7	9.1
Yttrium oxide, Y_2O_3	....	73.8	....	....	34.4	11.1	10.
Lead chromate, $PbCrO_4$	61.2	70.2	....	....	41.2	4.74	7.4
Aluminum oxide, Al_2O_3	....	84.1	87.7	....	20.8	2.34 1.64	6.5
Thorium oxide, ThO_2	....	86.0	....	....	46.9	7.11	10.0
Zinc oxide, ZnO	....	82.2	86.4	....	8.5	3.2 2.1	5.1
Magnesium oxide, MgO	....	86.3	....	....	16.0	2.5	9.1
Calcium oxide, CaO	....	85.4	....	....	22.3	3.6	6.2
Zirconium oxide, ZrO_2	82.2	85.8	84.1	83.2	23.2	5.1	5.4
Lead carbonate, $PbCO_3$	....	86.8 89.9	90.8 92.8 94.5	....	29.2	8.3 13.2	6.9
Magnesium carbonate, $MgCO_3$	....	85.2	89.4	....	10.8	4.1	8.8
White paper	....	71.7 73.4 for two thicknesses	74.7	....	18.2	5.0	....
White paper (Bond)	....	75.2	....	....	....	....	....
Feldspar, $KAlSi_3O_8$	....	....	86.7	....	38.2	10.3 14.6	9.7
Ibid (cleavage)	....	39.4	....	....	....	....	....
Bluestone (sandstone) SiO_2	....	....	18.4	....	8.1	17.6	11.0
Quartz (powder, French flint), SiO_2	....	....	81.0	....	41.5	7.9 13.4	9.0

TABLE V

Reflecting Power of Miscellaneous Substances

Wave length λ max.	0.60μ	0.95μ	4.4μ	8.8μ
Brick:				
Light buff	48.4%			
Darker	40.0			
Red brick	30.1			12.4
Darker and glazed	23.4			
White marble; $CaCO_3$; ground; unpolished	53.5		6.4	5.1
Ib d.; cleavage	40.8			
Indiana limestone; $CaCO_3$	42.9		20.3	5.0
Granolith (pavement)	16.9			
Asphalt (pavement)	14.8			
Ibid.; free from dust	7.2			
Slate (dark clay)	6.7			20.0
Blue flannel	17.5			
Black velvet	1.75		3.66	2.7
Black felt	13.9	21.2		
	22.5	25.6		
Deep blue cloth (Navy Dept.)	17.0			
Lighter shade	18.2			
Green leaf (tulip tree)	21.9	38.0	5.6	

TABLE VI

Reflecting Power of Dyed Cloth and White Paints

Wave length λ max	0.60μ	0.95μ	Wave length λ max	0.60μ	0.95μ
Linen; starched, dull finish	81.2%		Cotton cloth—Continued.		
White lead No 103	76.2	79.3	Diamine Aldehyde Black		
White lead No. 102	74.3		B—		
Zinc lead white No. 107	69.6		Pattern sheet No. 193	29.5	
Zinc oxide No. 104	68.1	72.1	Sulphur Black A W L—		
White lead 50% Zinc oxide 50% No. 209	70.8		Pattern sheet No. 192	2.43	2.57
			Ibid.; two layers	2.37	
Cotton cloth:			Woolen cloth:		
Diamine Fast Red, 8 B L—			Lanacyl Blue B N—		
Pattern sheet No. 187	43.8		Pattern sheet No. 189	25.1	
Diamine Fast Black C B—			Salacine Blue Black A E—		
Pattern sheet No. 186	33.1		Pattern sheet No. 193	14.6	17.8
Ibid.; two layers	33.5		Salacine Black P B—		
Columbia Fast Black R—			Pattern sheet No. 192	11.8	15.1
Pattern sheet No. 185	28.7		Ibid	13.2	

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INTRODUCTION

The demand for alcoholometric density tables of greater precision than those now in use has led to the experimental redetermination at the Bureau of Standards of the constants upon which such tables are based.

In order to provide the basis for the standardization of alcoholometers at this bureau, the work of preparing such tables was undertaken several years ago. Examination of the data then available showed that they were inadequate for the preparation of tables of the desired accuracy.

The scope of the present work includes the preparation of pure anhydrous ethyl alcohol, the determination of the density and thermal expansion of this alcohol and its mixtures with water, and the construction from these data of tables for convenient use.

The results of the density determinations by the authors are expressed in terms of the density of water at 4° C as the unit. The word "density" is employed throughout the paper in a general way as the name of the property of the substance; but where numerical values are given, whether those determined by the authors or quoted from other observers, the unit employed is either expressed in words or indicated by symbols.

The symbol $D\frac{t}{T}$ indicates the density of a substance at the temperature t in terms of the density of water under normal atmospheric pressure at the temperature T as the unit. The density expressed thus is equivalent to the ratio[a] of the density of the substance at $t°$ to the density of water at $T°$, and in the case where T equals 4° C the density is equivalent to density expressed in grams per millimeter. If not otherwise indicated, temperatures are on the centigrade scale, and for the experimental work presented here the International Hydrogen Scale of temperatures is used.

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[a] This ratio is often called "specific gravity."

PART 1

PREPARATION OF PURE ANHYDROUS ETHYL ALCOHOL

By E. C. McKelvy

The success of an attempt to prepare a pure material of any kind depends largely on its physical state at ordinary temperatures and on the limitations set by the nature of the physical properties, which may be determined in order to detect the impurities present. Generally speaking, chemical methods for detecting very small quantities of one substance in large quantities of another are rather poorly developed and unsatisfactory, especially in the field of organic substances. The present work presented the problem of preparing a pure liquid, ethyl alcohol, with many favorable conditions under which to work. The impurities contained in the product on the market are comparatively few, and there is no great difficulty in getting large quantities of the liquid containing 99.5 per cent ethyl alcohol. The problem resolved itself into a removal of the half per cent of impurity, mostly water, and the study of the variation of the physical properties of alcohol with small amounts of various impurities. The purification can be carried out by distillation at temperatures easily attainable, and the permissibility of working with large quantities of the liquid is a distinct advantage, especially in the preliminary purification. A considerable number of physical properties are applicable to the testing of the product, with, however, a large variation in their sensitiveness. It is evident that our knowledge of the purity of any material is subject to the limits set by the method of testing, whatever may be the efficiency of the method of purification.

I. HISTORICAL SURVEY

It was early appreciated that the most convenient basis upon which alcoholic liquors could be taxed was their alcohol content. The accurate determination of this value has occupied the attention of investigators for over a century, and several independent methods have been devised. A study of the literature on the subject will show that a number of physical constants have been proposed for this use. By far the larger bulk of the work, however, has had to do with the determination of the densities of alcohol-water mixtures, since a density determination gives an easy and accurate method of determining the alcoholic content of a liquor.

To utilize this method practically, it is of course necessary first to construct a table from density determinations on mixtures of known composition. In order that this may be done, it is essential that pure alcohol should be obtained. The efforts at the preparation of such an alcohol have been parallel with the development in the accuracy of alcoholometric tables. It is purposed to give a short historical survey of the main attempts to accomplish this result.

1. WORK BEFORE 1865—COMPARISON OF RESULTS.

It can be said concerning most of the results recorded before 1865, and of many since, that they are of limited accuracy, and hence of interest mainly from a historical point of view, notwithstanding that a part of this work forms the basis of the tables in current use. The main cause of this status is that the actual density determinations are generally given only to the fourth decimal place, and as a rule the results are poorly defined as to temperature conditions and bases of temperature and density references. A considerable part of this work has been briefly sketched in the papers of Mendeléeff [b, 207, 241] and Gerlach [445]. Blagden and Gilpin [4, 5] were among the first investigators to construct tables from actual density determinations. Their work was incomplete in that no success attended their efforts to obtain anhydrous alcohol, and so their results had only an arbitrary significance until the real alcohol value of their basis could be determined by later observers. The early attempts of Lowitz [10] and Richter [9, 11] to dehydrate alcohol, and the work of Tralles [30] have been thoroughly discussed by Windisch [684]. Table I will show the surprising agreement shown in the results of some of

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[b] Reference numbers printed in superior figures throughout this paper refer to "Bibliography," part 5, in which each title bears a specific reference number.

the experimenters working before 1865. McCulloch [106, 119] in a report to the Secretary of the Treasury of the United States reviews the work done up to that time, and on the basis of a few experiments and recalculations of his own recommends the alcoholometric tables for official use by the Treasury Department.

TABLE I

Density Determinations of Absolute Alcohol Prior to 1866

Name	Year	Dehydrater	Density value D_T^t	Basis of reference $\frac{t}{T}$	Density $\frac{20^\circ}{4^\circ}$ recalculated	Remarks
Blagden and Gilpin [4, 5]	1790 to 1794	None	0.825	$\frac{60^\circ}{60^\circ}$F	....	No dehydrating agent
Lowitz [10]	1796	K_2CO_3	.791	$\frac{16^\circ}{16^\circ}$C	0.7899	M.
Richter [9, 11]	1797	$CaCl_2$	.792	$\frac{20^\circ}{20^\circ}$C	.7909	M.
Saussure [17]	1807	$CaCl_2$	.792	$\frac{16^\circ}{16^\circ}$C	.7909	M.
Gay-Lussac [26]	1815	CaO	.7940	$\frac{15^\circ}{4^\circ}$C	.7898	M.
Meissner [27]	1816	$CaCl_2$	.791	$\frac{20^\circ}{20^\circ}$C	.7899	M.
Delezennes [28]	1823	....	.79370	$\frac{20^\circ}{0^\circ}$C	.79361	M.
Gouvernain [29]	1825	....	.79364	$\frac{16^\circ}{10^\circ}$R	.79348	M.
Dumas and Boullay [46]	1827	$CaCl_2$	.7915	$\frac{18^\circ}{x^\circ}$C	.7899	A.
Muncke and Gmelin [47, 48]	1828	....	.8062	$\frac{0^\circ}{4^\circ}$C	.7895	M.
Brown [49]	1829	....	.791	....	....	
Connell [68]	1835	CaO	.7938	$\frac{60^\circ}{x^\circ}$F	.7896	A. Assume x° = 60° F
Kopp [83]	1845	....	.80950	$\frac{0^\circ}{0^\circ}$C	.79277	M.
Pierre [84]	1845	CaO	.81508	$\frac{0^\circ}{4^\circ}$C	.79777	M. Pierre's expansion coefficient used
Fownes [90]	1847	CaO	.7938	$\frac{60^\circ}{60^\circ}$F	.78959	M.
Wackenroder [97]	1847	CaO	.7948	$\frac{21^\circ}{x^\circ}$C	.7905	A.

TABLE I—Continued

Name	Year	Dehydrator	Density value D_{T}^{t}	Basis of reference $\frac{t}{T}$	Density $\frac{20^\circ}{4^\circ}$ recalculated	Remarks
Drinkwater[163]	1848	CaO	0.793811	$\frac{60^\circ}{60^\circ}$F	0.78958	M.
Wetherill[160]	1848		.8194	$\frac{19^\circ}{X^\circ}$C	.8073	A.
Plücker[132]	1854	CaO	.792	$\frac{13^\circ.75}{X^\circ}$C	.787	A.
Delffs[128]	1854		.809	$\frac{5^\circ}{X^\circ}$C	.796	A.
Pouillet[152]	1859		.7947	$\frac{15^\circ}{15^\circ}$C	.7898	M.
Baumhauer[155]	1860	CaO	.7939	$\frac{15^\circ}{4^\circ}$C	.7897	A.
Mendeléeff[173]	1861		.7958	$\frac{15^\circ}{4^\circ}$C	.7916	A.
Gladstone-Dale[188]	1863		.7972	$\frac{20^\circ}{X}$C	.7929	A.
Landolt[190]	1864	CaO-Na	.8011	$\frac{20^\circ}{20^\circ}$C	.7997	A.
Mendeléeff[207, 241]	1865	CaO-BaO	.78945	$\frac{20^\circ}{4^\circ}$C	.78945	Uncorrected

EXPLANATION.—In the column headed "Remarks" M indicates that the densities at 20° were calculated by Mendeléeff. A indicates that this was done by the authors of this paper. Both calculations were made, except where otherwise stated, with Kopp's[92, 241] value for the expansion in the following formula:

$$D\frac{t^\circ}{4^\circ} = D\frac{20^\circ}{4^\circ} + (20^\circ - t^\circ)0.000846$$

where 0.000846 is the change in density for 1° C. X° signifies that the basis of density reference was not given and is assumed to be 4° in the recalculation. It is impossible to correct any of these values, except Mendeléeff's[207, 241] later one, to the international hydrogen scale of temperature.

2. WORK OF MENDELÉEFF (1865)

In 1865 Mendeléeff's [307] memoir on alcohol appeared in the original Russian and also in German. His experimental work is characterized by careful attention to details and skillful execution. The ethyl alcohol prepared by him was probably the purest prepared up to that time. His density values have been generally regarded with great confidence. Many of the generally accepted tables used in scientific work have as their basis Mendeléeff's value, with the application of certain well-defined corrections. Such are the tables prepared by Windisch,[995] using the value approved by the Normal-Eichungs Commission, Berlin; the tables given by E. W. Morley,[1060] using a value recalculated by himself; and the tables issued provisionally by the Bureau of Standards [1216] in 1909.

In Mendeléeff's work the first attempt was made to determine the relative efficiency of different dehydrating agents. From the results of previous investigators, as well as experiments of his own, he decided that such agents as anhydrous potassium carbonate, calcium chloride, and copper sulphate were unsatisfactory. Metallic sodium as such or in the form of an amalgam he found inefficient, an observation later substantiated by Squibb [483] and by Crismer.[1033] He concluded that lime, with the addition of a smaller quantity of baryta, was the most satisfactory means for dehydrating the alcohol. This addition of baryta had been recommended by Berthelot,[141] with the statement that the turning brown of the alcohol was an indication of complete dehydration, but it was later shown by Crismer [1033] that the baryta is unnecessary and undesirable.

In Table II are given the lowest density values found by Mendeléeff in his work with different dehydrating agents, certain of which are still in use. These results, if more generally known, would leave no doubt in the minds of chemists as to the agents which should be used if an alcohol as anhydrous as possible is desired. Table III contains the results of one of Mendeléeff's and one of Squibb's later distillations, showing the variation in the density of the different fractions. Unfortunately the volumes of the different fractions are not given.

TABLE II

Densities with Various Dehydrating Agents (Mendeléeff[207,241])

Dehydrator used	$D_{4^\circ}^{20^\circ}$	Remarks
K_2CO_3	0.78970	All distillations were made with the dehydrating agent present in the alcohol. No corrections have been applied to the results.
$CaCl_2$	.78960	
$CuSO_4$	.78961	
Na-Hg	.78974	
BaO	.789453	
CaO+BaO	.78945	

TABLE III

Variations in Density of Distillate Fractions

[Dehydrating agents: Mendeléeff, CaO+BaO; Squibb, CaO.]

Fraction	$D_{4^\circ}^{20^\circ}$ Mendeléeff[207, 241]	$D_{15^\circ6}^{15^\circ6}$ E. R. Squibb[673]	Remarks
1	0.78963	0.793960	These results are taken directly from the original articles without correction. The volume figures for the fractions are not available.
2	.78946	.793811	
3	.789442	.793639	
4	.789456	.793582	
5	.789442	.793576	
6	.789472	.793561	
7	....	.793499	

3. WORK SUBSEQUENT TO 1865

In Table IV are presented the results of most importance which have appeared since 1865. Table V shows the values obtained by other investigators during this period in cases where generally the density value was of secondary importance to the determination of other physical constants. In most of these cases no details of the density determinations are given.

TABLE IV

Ethyl Alcohol Density Determinations of Most Importance Subsequent to 1864

Name	Year	Dehydrator used	Density value given D_T^t	Basis of reference $\frac{t}{T}$	Density at 25° (calculated) D_4^{25}C
Mendeléeff [207,241]....	1865	CaO+BaO.........	0. 79358	$\frac{15^\circ}{4^\circ}$	0. 78504
Squibb, Messrs.[433]..	1884	CaO...............	. 79350	$\frac{15.6^\circ}{15.6^\circ}$	. 78470
Squibb, E. R.[679].....	1893	CaO...............	. 79350	$\frac{15.6^\circ}{15.6^\circ}$	. 78476
Cook and Haines [883].	1901	CaC_2...............	. 79357	$\frac{15^\circ}{4^\circ}$	. 78503
Young [906]...........	1902	Dist. w. hexane.....	. 80627	$\frac{0^\circ}{4^\circ}$	. 78507
Crismer [1008].........	1904	CaO...............	. 78746	$\frac{25^\circ}{25^\circ}$	. 78516
Winkler [1067].........	1905	Ca.................	. 78932	$\frac{20.07^\circ}{4^\circ}$	. 78510
Klason and Norlin[1100]	1906	Ca.................	. 79413	$\frac{15^\circ}{15^\circ}$	. 78490
Do.....................	....	Ca.................	. 78938	$\frac{20^\circ}{4^\circ}$	. 78508
Kailan [1148]..........	1907	CaO...............	. 78520	$\frac{25^\circ}{4^\circ}$	. 78520
Andrews [1167]........	1908	CaO, Ca, Mg-Hg...	. 78510	$\frac{25^\circ}{4^\circ}$	. 78510
Doroshevskii [1175]....	1908	CaO...............	. 79426	$\frac{15^\circ}{15^\circ}$	. 78503
Acree and Robertson [1267,1294]	1910	CaO...............	. 78506	$\frac{25^\circ}{4^\circ}$	. 78506
Doroshevskii [1269]....	1910	CaO...............	. 79412	$\frac{15^\circ}{15^\circ}$	. 78489
Röhrs [1296]...........	1910	Ca.................	. 795027	$\frac{14.2^\circ}{14.2^\circ}$	. 78521
Kailan [1341]..........	1911	CaO...............	. 78513	$\frac{25^\circ}{4^\circ}$	. 78513
Bureau Standards[1376]	1910	CaO, Al–Hg........	. 78506	$\frac{25^\circ}{4^\circ}$	. 78506

EXPLANATION.—Table IV represents an attempt to put the most important results for the density of anhydrous alcohol on a comparable basis. All reductions were made with the use of the formula obtained in Part II,

$$D^{t^\circ}_{4^\circ} = D^{25^\circ}_{4^\circ} - [859\ (t-25) + 0.6\ (t-25)^2 + 0.005\ (t-25)^3] \times 10^{-6}$$

and Chappuis's [1132] values for the density of water. The value given in Mendeléeff's original paper has been corrected to a more probable value for the density of water than that assumed by him and to the international hydrogen temperature scale.

TABLE V

Density Determinations of Secondary Importance Subsequent to 1865

Name	Year	Dehydrator	Density value D^t_T	Basis of reference $\frac{t}{T}$	Density at 25° (calculated) D^{25}_4
Linnemann [231].............	1868	K_2CO_3.......	0. 8086	$\frac{19^\circ}{19^\circ}$	0. 8022
Wüllner [234].................	1868	....	. 8133	$\frac{0^\circ}{x^\circ}$	. 7920
Darling [235].................	1868	....	. 8095	$\frac{0^\circ}{x^\circ}$	. 7926
Dupré and Page [237].........	1869	....	. 79792	$\frac{10^\circ}{x^\circ}$	. 78516
Do.....................	1869	....	. 79317	$\frac{15^\circ.5}{x^\circ}$	. 78509
Do.....................	1869	....	. 78932	$\frac{20^\circ}{x^\circ}$	. 78507
van der Willigen [245]........	1869	....	. 7935	$\frac{20^\circ}{4^\circ}$	. 7892
Pierre and Puchot [260].......	1871	....	. 822	$\frac{20^\circ}{x^\circ}$	. 818
Erlenmeyer [254].............	1871	CaO..........	. 79481	$\frac{11^\circ}{x^\circ}$	. 78291
Pierre [283]..................	1873	....	. 80214	$\frac{15^\circ}{x^\circ}$	. 79460
Winkelmann [284]............	1873	....	. 7946	$\frac{16^\circ.03}{4^\circ}$	. 78695

TABLE V—Continued

Name	Year	Dehydrater	Density value D^t_T	Basis of reference $\frac{t}{T}$	Density at 25° (calculated) D^{25}_4
Duclaux [312]	1877		0.7947	$\frac{15°}{4°}$	0.7860
Kundt [322]	1878		.800	$\frac{18°}{x°}$	.794
Brühl [343]	1880		.8000	$\frac{20°}{4°}$	.7957
De Heen [347]	1880		.7995	$\frac{14°}{x°}$	.7901
Lorenz [350]	1880		.7909	$\frac{20°}{x°}$	.7866
Vincent and Delachanal [359]	1880		.8120	$\frac{0°}{x°}$	.7908
Zettermann [362]	1880		.799	$\frac{17.°5}{x°}$	.793
Bedson and Williams [364]	1881		.8019	$\frac{20°}{4°}$	.7976
Drecker [400]	1883		.78962	$\frac{25.°42}{x°}$	.78998
Johst [406]	1883		.8072	$\frac{16.°7}{4°}$	.8000
Nasini [408]	1883	BaO	.7968	$\frac{20°}{4°}$	.7925
Quincke [411]	1883		.7969	$\frac{20°}{4°}$	.7926
Sieben [414]	1883		.796	$\frac{20°}{4°}$	.792
Perkin [431]	1884	$CuSO_4$	.78820	$\frac{25°}{25°}$	.78589
Kanonnikoff [449]	1885		.7918	$\frac{20°}{4°}$	.7875
Winkelmann. [462] (Kahlbaum's alcohol.)	1885		.7906	$\frac{20°}{4°}$	.7863

TABLE V—Continued

Name	Year	Dehydrator	Density value D^t_T	Basis of reference $\frac{t}{T}$	Density at 25° (calculated) D^{25}_4
Pagliani and Batelli [453]	1885		0.79175	18°/x°	0.78580
Worthington [463]	1885		.7906	25°.3/25°	.7885
Ketteler [531]	1888		.78987	20°/x°	.78562
Do	1888		.80681	0°/x°	.78560
Ångstrom. [512] (Air free)	1888		.80715	0°/4°	.78595
Ångstrom. (Air saturated)	1888		.80680	0°/4°	.78559
Hartwig [527]	1888		.7937	18°/4°	.7877
Le Blanc [563]	1889		.79643	20°/20°	.79076
Barbier and Roux [578]	1890		.805	14°/x°	.796
Buchkremer [581]	1890		.7935	20°/4°	.7892
Gartenmeister [584]	1890		.7943	20°/4°	.7900
Korten [588]	1890		.7910	20°/4°	.7868
Jahn [609]	1891		.79149	20°/20°	.78585
Schall and Koss'ky [622]	1891		.791861	18°/4°	.785883
Landolt and Jahn [646]	1892		.80197	17°.5/x°	.79557
Eykmann [659]	1893		.7963	12°.7/4°	.7856

TABLE V—Continued

Name	Year	Dehydrator	Density value D^t_T	Basis of reference $\frac{t}{T}$	Density at 25° (calculated) D^{25}_4
Edwards [692]	1894	....	0.7964	$\frac{20°}{15°.5}$	0.7914
Tammann and Hirsch'g [717]	1894	....	.7951	$\frac{15°}{4°}$	.7866
Lehfeldt [741]	1895	CaO-BaO ...	.7929	$\frac{18°}{4°}$	.7869
Sohet [818]	1897	....	.8089	$\frac{0°.9}{4°}$	.7885
Do	1897	....	.7711	$\frac{44°.7}{4°}$	.7879
Zecchini [832]	1897	....	.80513	$\frac{1°.8}{4°}$	.78546
Cohen [837]	1898	CaO.........	.8063	$\frac{0°}{x°}$	.7851
Tanatar and Klimenko [880]	1898	....	.79565	$\frac{15°}{x°}$	.78711
Loomis (Squibb).[920] (Determined by E. R. Squibb.)	1900	CaO.........	.79386	$\frac{15°.6}{15°.6}$	.78506
Carrara and Levi [949]	1902	....	.79425	$\frac{16°}{4°}$	.78741
Grunmach [950]	1902	....	.7888	$\frac{22°.8}{4°}$	.7862
Szilard [1083]	1905	CaO.........	.78990	$\frac{20°}{x°}$	.78565
Cheneveau [1133]	1907	....	.7886	$\frac{22°}{4°}$	.7860
Timmermanns [1162]	1907	....	.80664	$\frac{0°}{4°}$	.78544
Wagner and Schulze.[1164] (Alcohol from Winkler.)	1907	Ca...........	.793405	$\frac{15°}{4°}$	.78486
Getman [1183]	1908	....	.78684	$\frac{25°}{4°}$	.78684

TABLE V—Continued

Name	**Year**	**Dehydrator**	**Density value** D_T^t	**Basis of reference** $\frac{t}{T}$	**Density at 25° (calculated)** D_4^{25}
Herz and Kuhn[1187]	1908		0.7867	$\frac{25^\circ}{4^\circ}$	0.7867
Richards and Mathews.[1197] (95 per cent probably.)	1908		.8040	$\frac{20^\circ}{4^\circ}$	.7997
Rühlemann[1200]	1908		.7927	$\frac{20^\circ}{4^\circ}$	.7884
Turner[1208]	1908		.78948	$\frac{20^\circ}{4^\circ}$	.78520
Holmes and Sageman[1232]	1909	CaO	.78892	$\frac{25^\circ}{25^\circ}$	.78661
Dawson[1266]	1910		.791502	$\frac{18^\circ}{4^\circ}$	.78552
Polowzow[1292]	1910		.78970	$\frac{20^\circ}{4^\circ}$	.78542
Smits and de Leeuw[1308]	1910		.7907	$\frac{18^\circ}{4^\circ}$	.7847
Thole[1309]	1910	Ca	.7876	$\frac{25^\circ}{4^\circ}$	.7876
Warren[1322]	1910	CaO	.7940	$\frac{15^\circ}{15^\circ}$	.7848
Cederberg[1330]	1911		.7907	$\frac{19^\circ.5}{x^\circ}$	.7860

The density value obtained by Messrs. Squibb[483] is the lowest ever obtained. These investigators used freshly ignited lime as dehydrating agent. The treatment occupied several weeks and was made by percolation at ordinary temperatures. This work repeated by E. R. Squibb[679] 10 years later showed results only slightly higher. These authors concluded that they had not even then obtained anhydrous alcohol. The variation in density of their alcohol from that of Mendeléeff would represent an impurity of 0.03 per cent water in Mendeléeff's alcohol, assuming his higher value to be due to the presence of water. In the light of data to be presented later, it seems that these results can be explained on no other grounds than that in some way not known their standards of reference differed from those of other observers. In addition, there is some doubt concerning the precision of their temperature measurements. Cook and Haines[933] neglected to give their basis of density reference. On the assumption that this is water at its maximum density it is found to differ only slightly from the more reliable results. This is the only quantitative result obtained, so far as known, by the use of calcium carbide as dehydrating agent. Young,[986] without the use of chemical agents in the ordinary sense, obtained results in good accord with those of Mendeléeff. This was accomplished by distilling with benzene and with hexane. Crismer[1033] has shown the inefficiency of sodium and baryta as dehydrating agents and obtained his best alcohol by means of dehydration with lime. He also introduced the use of the critical solution temperature of alcohol-kerosene mixtures as a criterion of the water content of the alcohol. He concluded that its sensibility was of the same order as density determinations accurate to the fifth decimal place. Vandam[1130] in Holland and Andrews[1167] in this country have also made use of this criterion. The use of this constant promises to be of considerable importance both from the standpoint of convenience and range of applicability in determining the composition of water-alcohol mixtures.

Winkler[1087] obtained an alcohol of low density, using calcium to remove the water. Klason and Norlin,[1109] using the same agent after purifying by recrystallization of potassium ethyl sulphate according to recalculation in Table IV, get one result considerably lower than that of Winkler,[1087] or even the recalculated result of Mendeléeff.[207] However, the authors state that their results confirm the Windisch[685] basis, which is recalculated from the results of Mendeléeff, and also confirm the result of Winkler[1087] as opposed to that of Mendeléeff. These statements can be reconciled with each other and with the results gotten by recalculation, using the thermal expansion formula obtained in part 2, only by the consideration that the authors did not consider 0.05 per cent water, corresponding to 16 units in the fifth decimal place, as significant. The concordance between Mendeléeff's corrected value and Winkler's value is much better than between the latter and the result of Klason and Norlin. The result given under density $\frac{20^\circ}{4^\circ}$ calculated to 25° leaves nothing to be desired when compared with the results of most other investigators. There is some possibility of a misprint in the value at $\frac{15^\circ}{15^\circ}$. Kailan [1148, 1341] determined the conditions under which lime could be most effectively used as dehydrating agent, and later tried metallic calcium for removing the last traces of water. Andrews [1167] tested the relative effectiveness of lime, metallic calcium, and magnesium amalgam as dehydrators and obtained alcohols with each that differed only slightly among themselves and were only slightly higher in density than Mendeléeff's [207] generally accepted value. He used in addition to the density determinations the critical solution temperature and refractive index as criteria of complete dehydration. Extensive work has been done recently in Russia by Doroshevskii [1175, 1269] and collaborators on the physical constants of anhydrous alcohol and its mixtures with water. The density value shown in the table was gotten by dehydrating with lime. Among the physical constants considered were specific heat, refractive index, electrical conductivity, vapor pressure, and boiling points. Other alcohols were also studied. The difference in the two density values given for anhydrous ethyl alcohol by this investigator at different times represents 0.04 per cent water.

The determination of the influence of small quantities of water in ethyl alcohol upon the velocity of esterification by H. Goldschmidt and E. Sunde,[1101] and upon the velocity of other reactions by G. Bredig and W. Fraenkel,[1062], [1090] gives some promise of being of value in estimating the small quantities of water. J. Gyr [1186] has used this influence as a criterion in the dehydration of methyl alcohol. Millar [1288] and Braune [1329] regard this method as the best for detecting traces of water in alcohol. In the case of methyl alcohol and the esterification of phenyl acetic acid, assuming the same accuracy of temperature control, the greater accuracy of the density determination seems to just about counterbalance the great change in esterification constant for the same percentage of water content. However, the quantitative results are as yet too meager to allow of a certain conclusion in regard to the use of this constant. Kailan [1341] in a recent work shows the superiority of the density method in one special case. Acree [1357] and students, in velocity of reaction studies, have used an alcohol showing the same density as that obtained at this bureau. The effect of small quantities of water was small in alkaline solution but very marked in acid solution.

II. EXPERIMENTAL PART

1. OUTLINE OF WORK

This part of the work has to do with the preparation of chemically pure ethyl alcohol. Experimentally it was proposed: First, to obtain, if possible, using different methods of purification and dehydration, an alcohol showing constant physical properties, even though from different commercial sources; second, to use density determinations as the main criterion of the degree of dehydration and purity with the auxiliary use, in some cases, of the critical solution temperature of its mixtures with kerosene and of such chemical tests as can be applied; third, to obtain, if possible, an alcohol which on further treatment with dehydrating agents would show no decrease in density and no variation in the density of the various distillates from the beginning to the end of a distillation; fourth, to investigate the possible effect on the density of the impurities likely to occur. Aside from considerations having to do with alcoholometry, it was hoped that the additional information gained regarding the most efficient method for preparing pure alcohol, which as a solvent ranks next to water in importance, would be of some importance and value.

Full details of the density determinations are given on page 405 and following.

2. DETERMINATION OF THE CRITICAL SOLUTION TEMPERATURE

Alexejew,[404] Rothmund,[850] and Timmermans [1116] have worked extensively with the mutual solubility relations of two liquids. Consider curve III, Fig. 1, which represents the solubility relations between two components, A and B, partially miscible in the liquid state, dissolving in each other with an absorption of heat and the final disappearance of one of the liquid phases. The left-hand branch of the curve represents the solubility of A in B and the right-hand branch that of B in A. For constant temperature, below the maximum point of the curve, there are two liquid layers. At the maximum point the two layers become identical in composition. This temperature is called the critical solution temperature, and the concentration at this point is the critical concentration. The point X represents a divariant system. At the critical concentration and constant pressure the temperature is fixed, depending only on the nature of the components. This critical solution temperature is changed by the addition of a third component C, being fixed for fixed concentration of C. This change in the critical solution temperature by the addition of C has been applied with considerable success to the determination of the purity and composition of organic substances by Crismer,[1033] Timmermans,[1310] Andrews,[1167] and others.

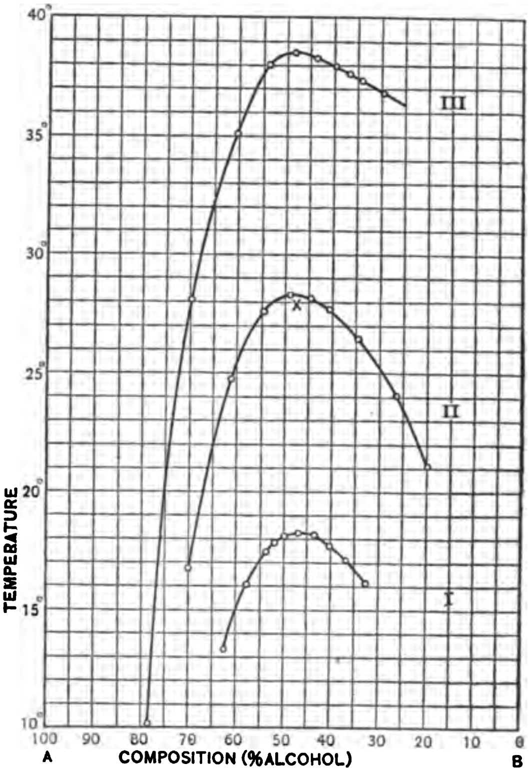


Fig. 1.—*Equilibrium diagram for system ethyl alcohol-kerosene*

Crismer [1033] found that the critical solution temperature of a binary mixture of ethyl alcohol and kerosene (considering a given kerosene as a component of constant composition) varied so considerably on the addition of water as a third component as to give results comparing favorably with the most careful density determinations for a criterion of the water content of an alcohol-water mixture. This work was later substantiated by Andrews.[1167] In the present work the results of Crismer were again substantiated and the valuation of this constant for alcohols containing very small amounts of water proved of considerable importance in testing the fractions of several of the distillates. The variation of the critical solution temperature as a function of the amount of water present is given in curves of Fig. 2, with a comparison of our own results with those of Vandam [1130] and Andrews [1167] obtained with different kerosenes.

Curve I (Fig. 2) represents the results of Vandam and Curve IV those of Andrews. They are in very good agreement. Curves II and III show the results of the present work. Only mixtures with small amounts of water were investigated. In order to make this physical constant of value over a large range of compositions, it would be necessary to have a series of oils so chosen as to keep the critical solution temperatures within the range of ordinary temperatures most easily observed. The variation for 1 per cent of water can be read from the curves.

Curves II and III are for oils A and B, respectively (p. 347). The results indicate a large variation of the critical solution temperature caused by small quantities of water, and this variation is independent of the nature of the oil used.

As pointed out by Crismer, the temperature requires to be determined to 0°.05 to give the same precision as density determinations to the fifth decimal place, which requires temperature regulation to 0°.01 or 0°.02 in making density determinations. As shown in Fig. 1, the critical concentration was determined by determining the solubility curves. The maxima of the solubility curves for alcohols containing small amounts of water are not shifted appreciably with respect to the alcohol-oil composition. In Fig. 1, considering the concentration of the water as being measured along an axis perpendicular to the plane of the paper, the upper Curve III represents the projection of the real solubility curve upon the plane of the paper, which is the zero water plane.

Curve I (Fig. 1) shows the solubility curve obtained with oil B and alcohol V–2, a distillate shown in Table X. Curve II represents the solubility relations of oil A and alcohol IX–5 of Table XIII. Curve III gives the curve for oil A and an alcohol IX–0 before dehydration. Since the maximum of the curve is higher than the value given in Table XIII, the sample evidently absorbed additional moisture during the time between the two determinations.

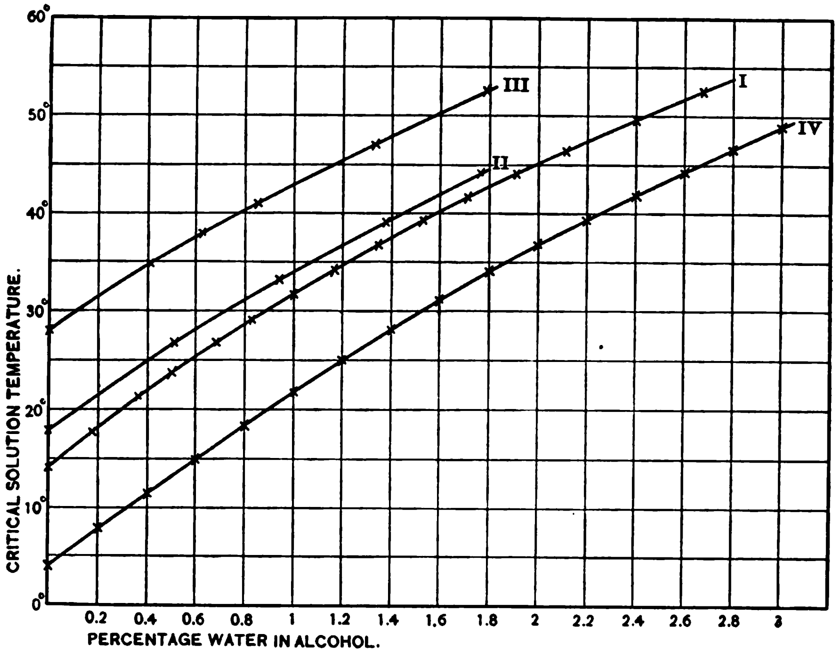


Fig. 2.—*Change of critical solution temperature with varying water content of ethyl alcohol*

In the determination of the critical solution temperatures equal volumes (generally 5 cc) of the alcohol and the kerosene were placed in a small bulb, care being taken to exclude moisture. This was warmed to the region of complete miscibility and slowly cooled in a bath the temperature of which could be varied at any desired rate. At the critical solution temperature there is a sharp cloud formation. No difficulty was experienced in repeating observations to 0°05 C. In this system there was no disturbing critical opalescence at the critical concentration. In the solubility-curve determinations the end point was not so sharp for the concentrations containing a large percentage of oil.

Kerosene is especially adapted for use as one of the components, since it can be so chosen or changed by mixing with lighter hydrocarbons that the value of the critical solution temperature will be such as to permit convenient temperature measurements. Two kerosenes were used, which will be designated as oil A and oil B.

Oil A had a critical solution temperature with anhydrous alcohol of 28°3. Slow changes in this value took place when the oil was dried over sodium. It was found that a lower and more constant value could be obtained if the oil were dried over anhydrous calcium chloride. The changes are probably due to the chemical action of the sodium on the oil.

Oil B was made by diluting oil A with a lower-boiling kerosene. With anhydrous alcohol it gave a critical solution temperature of about 18°0. The oil had a density at 25° of 0.8102, was dried over anhydrous calcium chloride, and its composition as determined by check determinations with anhydrous alcohol remained unchanged over a period of several months. The preliminary experimental work showed that equal volumes of the two liquids were sufficiently near the critical concentration to permit this concentration to be used for all determinations of the critical solution temperature of alcohols containing very small amounts of water and where the relative values are of most importance. The percentage concentration by weight of alcohol in such a mixture with oil B was 49.2 per cent. Examination of the curves will show this to differ very little from the critical concentration as shown by the maxima of the solubility curves.

In certain of the experiments the values for the critical solution temperature are given in comparison with the density values.

3. MATERIALS

Purification and dehydration experiments were made on four samples of alcohol of different commercial origin. These will be designated as samples A, B, C, and D. Sample A was purchased from Iler & Co., The Willow Springs Distillery, Omaha, Nebr., and is known to the trade as "silk-finished spirits." From density determinations, this alcohol showed a percentage strength by weight of 92.8, and it was used in most of the experimental work. An analysis made at this bureau gave the following results:

	Per cent.
Aldehydes (as acetic aldehyde)	0.0027
Methyl alcohol (Trillat[863, 864] method and Mulliken and Scudder[895, 922, 1082] method)	None.
Furfural	0.00015
Fusel oil (as amyl alcohol), Allen-Marquardt[380] method	0.033

No methyl alcohol was found by the same methods in the first distillate from 4 liters. Methods of analysis of Association of Official Agricultural Chemists[1265] were used. This analysis shows the sample to have a satisfactory purity for a material with which to start a further extended purification.

Sample B, of approximately the same strength as sample A, was obtained from the Columbia Distilling Co., and showed a satisfactory purity.

Sample C consisted of Squibb's absolute alcohol, having a density of 0.78570 at 25° C., corresponding to 99.8 per cent on the basis of the Bureau of Standards tables.[1216] This alcohol was several years old, and qualitative tests showed it to contain considerable aldehyde. It also possessed a foreign aromatic odor.

Sample D consisted of Merck's absolute alcohol Ph. IV, having a density of 0.78705 at 25° C., corresponding to 99.3 per cent. This sample contained considerable amounts of aldehyde, and was used directly in a final distillation without preliminary dehydration and purification.

4. PURIFICATION AND TESTING FOR IMPURITIES

In the preliminary purification attempts to remove the last traces of aldehyde by the method of Winkler[1087] were unsuccessful, both at ordinary and the boiling temperature. Considerable amounts were removed in this way, but no part of the distillate was found entirely free from aldehyde. No attempt was made to remove the higher boiling impurities other than water, except by rejecting the first and last tenths of the distillates.

Sample A was treated with silver oxide in alkaline solution under the reflux condenser for several hours and then distilled. Sample B was treated in the same manner in the presence of considerable amounts of lime, in order to dehydrate at the same time. Sample C was treated with silver oxide in alkaline solution at room temperatures, the clear liquid decanted and distilled, and then subjected to the final distillation. In all preliminary dehydrations the great bulk of the impurities were rejected in the first and last tenths of the distillate. With samples A and B it was possible by means of one dehydration with lime, in the proportion recommended by Kailan[1148] (550 grams per liter), to obtain large quantities of alcohol having a density of 0.78961 at 20° C, corresponding, according to the Bureau of Standards[1216] tables, to 99.9 per cent alcohol by weight. This still contained minute traces of aldehyde, the impurity most easily detected. The method of aldehyde removal with metaphenylenediamine hydrochloride, suggested by Windisch[483], was not used because of the danger of introducing into the alcohol even more objectionable impurities. The last traces of aldehyde were successfully removed by the method of Paul[778]. The alcohol was boiled for several days under a reflux condenser, coming in contact with nothing other than glass and dry air. The cooling water in the condenser was held at a temperature varying between 50° and 60° C. The top of the condenser was provided with an arrangement by means of which the more volatile constituents could be drawn off by means of a current of dry air. This arrangement is shown in Fig. 4. At the end of such a treatment, lasting two days, no more aldehyde could be found in the vapors drawn off and the most delicate tests failed to reveal it in the alcohol. During this procedure the alcohol did not change a determinable amount in density, as shown by determinations made before and after the experiment. There was some indication of aldehyde formation when the aldehyde-free alcohol was exposed to diffused daylight for a few hours. After keeping in the dark for a week, tests showed about as much aldehyde as was present before the treatment.

In general, it seemed that chemical methods for removing aldehyde depending upon its oxidation to the corresponding acid were useless in entirely removing the aldehyde. It seemed hardly possible that an agent could be found which would oxidize aldehyde completely without attacking alcohol in the least. Agents such as silver nitrate, silver oxide, and potassium permanganate certainly fail. Metaphenylenediamine hydrochloride is very efficient in case a water-free alcohol is not desired. There has been very little work done on the efficiency of the opposite procedure—that is, reduction of the aldehyde to the corresponding alcohol. According to Wurtz [181] ethyl alcohol can be prepared by reducing acetaldehyde with sodium amalgam. It was hoped that in the use of aluminum amalgam as a dehydrating agent it would also prove a means of removing the last traces of aldehyde. In view of the consideration that a small quantity of aldehyde is probably formed in the dehydration and in view of the above experiment and additional ones to be given later, showing its small effect on the density, it was not deemed worth while to make absolutely sure that the dehydration experiments were started with a strictly aldehyde-free alcohol.

In general, the final distillates were tested for the impurities likely to occur, such as aldehydes, the higher alcohols, ether, and water. A brief description of the procedures found most satisfactory follows.

Tests for Aldehydes.—From among the various tests for the lower aldehydes the sulphite-fuchsine reaction was found to be the most sensitive and reliable. Ammoniacal silver solution, silver nitrate solution, the Windisch reaction, using metaphenylenediamine, and the Fischer-Penzoldt [410] test, using diazobenzene sulphonic acid, were not found satisfactory, either because of lack of sensitiveness or of the interfering action of the alcohol itself. The sulphite-fuchsine test as proposed by Schiff [300] and further developed by Gayon [493] and Paul [778] was found fairly satisfactory for small amounts of aldehyde in alcoholic solution. The reagent was made up according to the method of Paul [778], using sulphurous acid to decolorize the fuchsine, and all tests were made with close adherence to his procedure. The relative results on the aldehyde content of the various fractions are given in some of the experiments. There is, however, some uncertainty as to the absolute amount of aldehyde present. In some fractions it was impossible to get a positive test for this impurity, and it is safe to say that in the fractions showing the strongest test the amount of aldehyde was less than 0.001 per cent, and so of neglible effect on the density. Experiments made with water solution of formaldehyde showed that by means of this reaction one part in a million could just be detected. The sensitiveness is decreased by the presence of alcohol on account of the uncertain action of pure alcohol itself on the reagent.

Tests for Higher Alcohols (Fusel Oil).—The quantities of any higher alcohols present were so small as to escape detection by any of the ordinary quantitative methods. After the preliminary purification and one distillation no color was given on standing for a week mixed with an equal volume of concentrated sulphuric acid. It was reasonably concluded that the alcohol was free from higher alcohols in any quantity sufficient to affect the density, outside the limits of the experimental error in its determination.

Other Possible Impurities.—It was considered unlikely that ethyl ether was present, though theoretically a further treatment with a strong dehydrating agent could possibly take from the chemical compound ethyl alcohol (C_2H_5OH) the constituents of water, forming the ethyl oxide $(C_2H_5)_2O$. In the absence of any reliable chemical test for small quantities of ether in the alcohol it was concluded that any appreciable quantity would, on account of its much lower boiling point, show in the first distillate and be recognized both by odor and by a different density. It was deemed unnecessary to consider testing for such unlikely impurities as methyl alcohol and acetone which could not be found in the original samples of alcohol.

Tests for Water.—No specific chemical test for water in such small quantities as they existed in the distillates was found to be of any value. Mendeléeff [207, 241] found barium oxide, zinc ethyl, and sodium amalgam unadapted to detect traces of moisture in alcohol. The test with lead-potassium iodide suggested by Biltz [1129] was found to be inapplicable to alcohol. Such agents as calcium carbide, anhydrous copper sulphate, and metallic calcium gave no indication of water with alcohols whose density at 25° C was below 0.78510.

The determination of certain physical constants is the most satisfactory test for and criterion of the water content. The only objection to such criteria is the necessary assumption of the absence of other substances in quantities sufficient to affect the physical constant determined. Making this assumption then, the determination of physical constants becomes the only satisfactory method for determining quantities of water so small. Since this work has to do with the establishment of a firm basis for density alcoholometric tables, the determination of the density was taken to be the main criterion of the water content.

A detailed description of the methods employed in the density determinations and the data on the determinations which were chosen as establishing the density of absolute alcohol will be found in part 3 of this paper (p. 405). It having been there shown that a knowledge of the condition of saturation of the alcohol with air is essential in order to use density as a criterion of dehydration, the densities given here are for alcohol saturated with air at the temperature of the determination.

Some use was also made of the determination of the critical solution temperature as a second criterion. The best criterion of the attainment of a chemically pure anhydrous ethyl alcohol was the obtaining of a considerable sample, which on further treatment with the same dehydrating agent gave a distillate with the same density from beginning to end of distillation and a value very close to that obtained from various samples of alcohol and by using various efficient methods of dehydration.

5. DEHYDRATION AND DISTILLATION OF THE ALCOHOL

Dehydrating agents.—Such reagents as potassium carbonate, sodium amalgam, anhydrous copper sulphate, and calcium chloride were rejected. Calcium carbide was not used because of the possibility of introducing organic impurities impossible to remove. On long contact with alcohol many decomposition products are formed. Lime with the addition of a small quantity of barium oxide was used in an exact duplication of Mendeléeff's [207, 241] treatment. The larger number of distillations were made with lime alone, using samples as obtained on the market, and also these same after being freshly ignited. Repeated distillation of the same sample of alcohol was made with this reagent. The efficiency of metallic calcium was also tested and found satisfactory when used in small amounts. Aluminum amalgam was used for the first time in a quantitative test of its efficiency and some of the best alcohol was obtained in this way.

Apparatus and Procedure.—The various distillations were carried out in three types of apparatus. For convenience they will be designated by the letters *L*, *M*, and *N*. The first type of apparatus, *L*, was used in all preliminary distillations and some of the earlier ones of which the results are recorded. It consisted of a 5-liter Jena flask provided with a 40-cm Hempel still-head filled with short pieces of glass tubing. To this was connected an 80-cm condenser provided with several interchangeable 500-cc flasks as receivers. These were amply protected from the moist air by means of calcium chloride tubes. The connections between the various parts were made with corks covered with tin foil and there was present the possibility of the introduction of appreciable impurities from these. The second type, *M*, was used in the distillations carried out under reduced pressure. The necessary connecting corks were in this case paraffined and the joints made

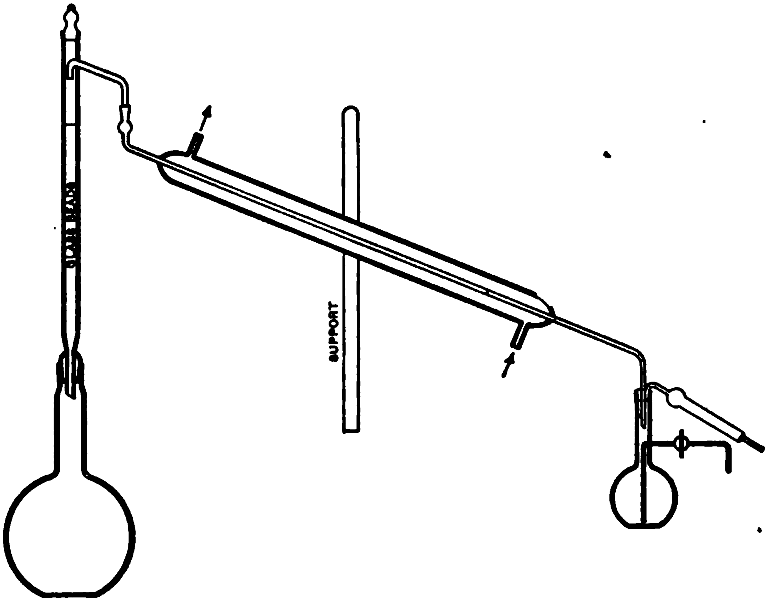


Fig. 3.—*Distilling apparatus—Type N*

tight by means of mercury seals. The distillations were made from 2 and 3 liter round-bottomed flasks. The pressure could be reduced to 80 mm, giving a boiling temperature of about 40° C.

The third type, *N*, is shown in Fig. 3. In this apparatus the greatest efforts were made to exclude the possibility of moisture or other impurities being introduced. The still was made entirely of glass, the connecting joints being ground accurately. Distillations were made from 3- and 5-liter flasks into the 500-cc receiver. Any fraction of the total distillate under 500 cc could be siphoned off. The entire system was protected from the entrance of moisture by calcium oxide guard tubes. Fig. 4 shows the reflux condenser, used in connection with this apparatus, for the heating of the alcohol with the dehydrating agent and the carrying out of Paul's procedure of removing the aldehyde or other volatile impurities.

All preliminary distillations were made with apparatus *L*, distilling from a water bath varying in temperature between 80° and 90°. All the distillations carried out with the hope of getting an anhydrous alcohol were made from an oil bath consisting of a high grade and high boiling lubricating oil giving off no appreciable vapors below 110°. The temperature of this bath, which was heated electrically, varied in the experiments between 80° and 110°.

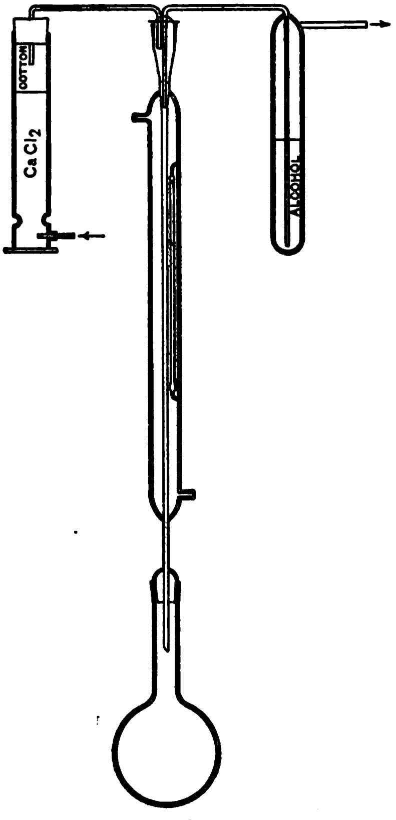


Fig. 4.—*Reflux apparatus*

The following precautions to prevent moisture absorption by the alcohol were taken in all the final experiments of which the results are given. In all cases of heating under the reflux condenser the exit was provided with lime or calcium chloride guard tubes or a moving current of dry air. Immediately before putting the still head, with condenser and receiver attached, in place of the reflux condenser, the entire apparatus was swept out for 10 minutes by a stream of air thoroughly dried by passing through a calcium chloride drier, sulphuric acid, and over phosphorous pentoxide in succession. The only time during which the vapors of the alcohol came in contact with the outside air was during this transfer, which occupied about five seconds. All retainers for the distillate were swept out in the same way. The various fractions, in case they were not used at once, were always kept in tightly stoppered bottles inclosed in large lime desiccators. The alcohol at no time came in contact with moist air or any glass surface that had not been dried by means of a current of dry air. In a few distillations which will be mentioned small quantities of the dehydrating materials were placed in the still head so that the vapors of the alcohol would come in intimate contact with the same immediately before passing into the condenser. All dehydrating agents were made as nearly anhydrous as possible before any attempt was made to use them. The details of their preparation will be given under the separate experiments to be described.

6. EXPERIMENTS AND RESULTS

Fourteen separate dehydrations and distillations were made. These will be designated by Roman numerals. The following outline of the subject matter of their description is given for the sake of clearness. For each of these it is proposed to give—

1. Type of distilling apparatus used, the sample of alcohol used, its density, and, as far as needed, its previous history.
2. The preparation of the dehydrating agent, the treatment of the alcohol in dehydrating, and any special features of the distillation.
3. The results in a tabulated form, giving the number of fractions, their volume, the time occupied in their distillation, and their density at 25° compared with water at 4°, and the critical solution temperature when determined. Some density values at 15° will be given. Considering the fact that a change in density

of 0.000010 corresponds to a temperature change of only 0°012, the reader will not give undue significance to the sixth decimal place, which is here given for purposes of comparison.

4. A short discussion of the more specialized features and results of a given experiment.

Experiment I.—Three and one-half liters of alcohol from sample A were distilled in apparatus *L*. This alcohol had been dehydrated with lime and showed a density of 0.78961 at 20° C. It was also free from aldehydes. On standing for five days, protected from daylight in contact with 700 g of ordinary commercial lime, it assumed a lemon-yellow color. About 100 g of barium oxide were added and the whole heated under the reflux condenser for 10 hours. The alcohol turned a deep brown color. Immediately before the distillation 50 g of finely powdered lime were added in order to take up any water produced by the too extensive formation of barium alcoholate. This formation of water was shown by Crismer.[1033] The barium oxide was added merely with the purpose of carrying out one distillation, following as closely as possible the procedure of Mendeléeff.[207, 241] Subsequent experiments show that it can be dispensed with, and it is certainly undesirable to have such extensive reactions, foreign to the purpose of dehydration, going on during the process.

TABLE VI

Results of Experiment I

Sample	Volume	Time	$D\frac{25°}{4°}$
	cc	hrs	
Original	3500	....	0.78535
Fraction:			
1	1000	9	.785153
2	500	3	.785081
3	500	3	.785066
4	350	2	.785062
5	300	6	.785063
6	350	9	.785061
7	250	2	.785060
8	125	3	.785072

Though the original alcohol used was entirely free from aldehyde, small quantities were found in all the distillates with the minimum amounts in the middle fractions. Evidently they were produced during the dehydration process. In no case was the content above 0.001 per cent. This experiment is a very satisfactory reproduction of the work of Mendeléeff, the results agreeing with his as to the value of the density, but at the same time showing a much greater uniformity in the various fractions. While the last fraction was being distilled the oil bath was at a temperature of 100°. This fact, in conjunction with later experiments, shows that the temperature of the heating bath has little to do with the composition of the distillates when distilling a nearly anhydrous alcohol, provided it does not exceed 110°. Within the limits tried the rate of distillation seems to have no disturbing influence. The rate was varied from 40 to 175 cc per hour without any significant change in the density values.

Experiment II.—Three liters of sample A, having a density of 0.78961 at 20° C, after preliminary dehydration, were treated with lime, duplicating as closely as possible the procedure of Messrs. Squibb.[403] The distillation was carried out in apparatus *M* under reduced pressure, varying between 80 and 100 mm, necessitating a bath temperature between 35° and 45°. Air-slaked lime in powdered condition was ignited at a red heat for 10 hours and let cool in dry air. This, with some large pieces of freshly ignited lime, aggregating about 400 g per liter of alcohol, was rotated in the cold for three days and let stand for six weeks with frequent shaking. The clear lemon-colored liquid was siphoned off and distilled.

TABLE VII

Results of Experiment II

Sample	Volume	Time	$D\frac{25^\circ}{4^\circ}$
	cc	hrs	
Original	3000	....	0. 78535
Fraction:			
1	500	1	. 785097
2	500	1	. 785088
3	500	3	. 785085
4	500	3	. 785107
5	500	3	. 785101

The fractions from this distillation contained traces of aldehyde. By dehydration and treatment essentially similar to that described by Messrs. Squibb, it was not possible to duplicate the low values gotten by them for the density of anhydrous alcohol. The values, on the other hand, agree with those obtained by other investigators using a great variety of dehydrating agents. The slightly higher values of all the fractions may be due to their containing less dissolved air.

Experiment III.—One liter of lot C of Squibb's manufacture, after the preliminary purification had reduced the foreign odor and removed the bulk of the aldehyde content, was treated with 400 g of freshly ignited lime in apparatus *N*. It was subjected to Paul's[778] treatment in order to remove any of the more volatile constituents still remaining.

TABLE VIII

Results of Experiment III

Sample	Volume	Time	$D\frac{25°}{4°}$
	cc	hrs	
Original	1000	....	0.78570
Fraction:			
1	500	3	.785072
2	200	1	.785070

The results of this experiment show the efficacy of Paul's procedure in removing the lower boiling impurities. In the distillates the foreign odor and the aldehyde were just noticeable. The values are very close to what appears to be the normal one.

Experiment IV.—This experiment was intended to represent our best efforts in obtaining a pure anhydrous alcohol and was carried out with every precaution that occurred to us. Three and three-tenths liters of mixed distillates from previous experiments were treated in apparatus *N* with 500 g of lime made from marble. This lime was ignited for 10 hours in an electrical resistance furnace at from 600° to 700°. After the mixture had been left standing for three days at room temperature, with frequent shaking and after the addition of 25 g of powdered lime that had been ignited to 900° for 24 hours, the whole was heated under the reflux for 10 hours. The same amount was added immediately before distilling. A considerable quantity of small chips, ignited in the same way, was put into the still head and the distillation begun before the alcohol had cooled. Fractions were taken directly from the receiver into the tube in which the density determinations were made. The distillate was so divided into fractions as to show the possible differences in the physical properties of its parts to best advantage.

The results show the distillate to have been very nearly uniform throughout. The density at 25° of fraction 2 on keeping for several months in a glass-stoppered bottle in a lime desiccator that was frequently opened changed to 0.785088, representing an absorption of 0.006 per cent moisture, assuming no other changes in the alcohol of such a nature as to influence the density.

TABLE IX

Results of Experiment IV

Sample	Volume	Time	$D_{4^\circ}^{25^\circ}$
	cc	hrs	
Original	3300		0.785116
Fraction:			
1	120	0.5	.785097
A	450	1.5	
2	120	.5	.785069
B	500	1.0	
3	120	.5	.785058
C	350	.5	
4	120	.5	.785056
D	350	1.0	
5	120	.5	.785056
E	400	1.0	
6	450	1.0	.785054

Omitting the density value of the first fraction the various fractions have the same density to within two units in the fifth decimal place.

Experiment V.—Four liters of sample B, comprising the middle fractions from the preliminary dehydration and purification, were added to the residues and lime of Experiment IV in the same apparatus.

Heating under the reflux was continued for a week with the water in the reflux between 50° and 60°. The still head containing the chipped lime was again used.

TABLE X

Results of Experiment V

Sample	Volume	Time	$D_{4^\circ}^{25^\circ}$
Fraction:	cc	hrs	
1	400	1	
2	1000	3	0.785051
3	2100	4	.785101
4	200	1	

These distillates contained no aldehyde. They were used in subsequent experiments to test the effect of successive dehydrations and the use of calcium. Freshly ignited lime does not seem to be necessary in order to obtain an alcohol of very low density.

Experiment VI.—The third fraction of 2000 cc from Experiment V was distilled from apparatus *N*. This alcohol was treated with about 400 g of commercial lime taken from large pieces and the whole heated under the reflux for 18 hours. The middle fraction of 1250 cc showed a density of 0.785058 at 25°.

It appears from this experiment that a repetition of the dehydration even with commercial lime reduced the density of the alcohol product considerably.

Experiment VII.—The middle fraction of Experiment VI was treated with 150 g of chipped lime that had been ignited at 900° for 10 hours. This was heated under the reflux for 18 hours and then distilled in apparatus *N*.

TABLE XI

Results of Experiment VII

Sample	Volume	$D_{4^\circ}^{25^\circ}$
	cc	
Original	1250	0.785058
Fraction:		
1	120	.785064
A	250	
2	120	.785059
B	120	
3	120	.785060

This is the final of three successive dehydrations of the same sample of alcohol with lime. The value remains essentially unchanged and the separate fractions show a remarkable agreement in their densities, indicating the purity and uniformity of the alcohol. It seems that this distillate represents the best results obtainable with lime as a dehydrating agent, and also from the standpoint of uniformity of the different parts of the distillate. It is probable that this alcohol is freer from impurities than any obtained in this work with the possible exception of the distillates of Experiment XII.

Experiment VIII.—The combined fractions from Experiment VII, aggregating about 750 cc, were treated in apparatus *N*, with 6 g of metallic calcium and let stand over night. The calcium acted upon the alcohol with hydrogen evolution giving a white crystalline alcoholate, which went into solution on raising the temperature.

TABLE XII

Results of Experiment VIII

Sample	Volume	Time	$D\frac{25°}{4°}$
	cc	hrs	
Original	750	....	0. 785061
Fraction:			
1	250	3	. 785081
2	250	1. 5	. 785072
3	200	2	. 785080

The table shows a slight increase in the density results. This can not be certainly ascribed to an increase in the water content. It may easily be due to a variation in the condition with regard to air saturation caused by the calcium treatment or to the formation of a small quantity of some other substance. The residues in the flask were brownish. The distillation was carried almost to dryness. Other investigators have found smaller amounts of calcium more efficient than large amounts. The value obtained for the density by use of this agent is lower than that obtained by other investigators, excepting Klason and Norlin.[1100] Results indicate that lime is more efficient than metallic calcium.

Experiment IX.—Four liters of sample D without preliminary dehydration and purification were treated with 400 g of recently ignited lime per liter of alcohol. This was let stand for several weeks with frequent shaking. As in the other cases of dehydrating with lime, a lemon yellow color appeared, deepening finally to a brown. No attempt was made to remove the aldehyde by chemical means. The whole was subjected to Paul's[778] treatment of boiling under the reflux for about two days. Distillation was carried out in apparatus *N* after adding about 25 g of freshly ignited powdered lime.

TABLE XIII

Results of Experiment IX

Sample	Volume	Time	$D\frac{25°}{4°}$	Critical solution temperature
	cc	hrs		°C
Original	4000	....	0.787048	37.60
Fraction:				
1	120	1.5	.785128	18.45
A	500	1.5	....	
2	150	.5	.785078	18.25
B	500	1.5	....	
3	200	.5	.785067	18.30
C	500	2.0	....	18.25
4	120	.5	....	18.10
D	500	3.0	....	18.20
5	150	3.0	.785048	18.17
E	500	3.5	....	18.15
6	500	6.5	.785101	18.30

In the last column are given the values of the critical solution temperature. The relative values of this constant found for the different fractions are somewhat irregular, but in general follow the density values. By one dehydration with lime of a commercial absolute alcohol as above it is possible to get a middle portion of the distillate showing the density value of anhydrous alcohol. This alcohol from a different commercial source furnishes anhydrous alcohol of essentially the same physical properties as the other samples examined.

Experiment X.—The three following experiments were made, using activated aluminum (aluminum amalgam) as dehydrating agent. There are several statements in the literature regarding its efficacy, but no quantitative experimental data.

One liter of sample A, having a density of 0.78535 at 25°, after the preliminary dehydration, was treated with 10 g of aluminum amalgam. The distillation was carried out in apparatus *M* under reduced pressure. The amalgam was prepared as recommended by Wislicenus and Kaufmann[76] by etching aluminum wire with sodium hydroxide solution and then treating with a dilute solution of mercuric chloride. The amalgam, after washing with alcohol and ether and subsequent drying, was let stand with the alcohol over night. There was an abundant formation of the insoluble alcoholate with copious hydrogen evolution.

TABLE XIV

Results of Experiment X

Sample	Volume	Time	$D\frac{25°}{4°}$
	cc	hrs	
Original	1000	....	0.78535
Fraction:			
1	500	4	.785112
2	300	2	.785077
3	100	1	.785088

Twenty cubic centimeters of fraction 2 were added to fraction 3 to give sufficient volume for the determination of the density.

Experiment XI.—One liter of the same sample as used in the previous experiment was treated with 10 g of amalgam and let stand for three weeks. This amalgam was made by heating the wire in mercury up to the boiling point of the latter. The distillation was carried out in apparatus *M* under reduced pressure. After rejecting the first 50 cc the middle fraction of 400 cc showed a density, at 25°, of 0.785089.

Experiment XII.—Two and one-half liters of sample A, after preliminary purification, were treated with amalgam made from 25 g of aluminum wire. The alcohol was kept boiling for a week under a reflux condenser containing water varying in temperature between 50° and 60°. No aldehyde was contained in the vapors drawn off at the end of this treatment. Immediately before distilling in apparatus *N* some freshly amalgamated wire was placed in the still head.

TABLE XV

Results of Experiment XII

Sample	Volume cc	$D\frac{25^\circ}{4^\circ}$
Original	2500	0.78535
Fraction:		
1	250	.785056
2	250	.785068
3	500	.785051
4	350	.785051
5	250	.785061
6	300	.785056

The alcohol obtained in this experiment represents a pure liquid within the limits set by the sensitiveness of the density determination as a criterion of purity. The density results agree very closely with those obtained by other methods of dehydration. All the fractions were practically free from aldehyde. The amalgam may act as a reducing agent, converting aldehyde into the corresponding alcohol or at least preventing any formation of aldehyde during the dehydration.

Experiment XIII.—In order to furnish anhydrous alcohol for a check series of density determinations of mixtures given in part 4, two additional distillations were made.

Two liters of a mixture made from fractions of various distillations of lots A and B (IV, 1; V, 4; VI, 1; XII, 1, 6) were treated with 200 g of freshly ignited lime. The alcohol was let stand for 10 days with frequent shaking. The clear liquid was siphoned off with careful exclusion of moist air and treated under the reflux condenser for a day after adding 50 g of freshly ignited, air-slaked lime which was in a very fine state of division. The water in the reflux was held at about 60° and the more volatile constituents were removed by means of a moving current of dry air led into the top of the condenser. Fifty grams additional of powdered lime were added immediately before distilling. Apparatus *N* was used with the receiver directly sealed to the condenser. The densities of the various fractions were determined at 15° in order to give a direct comparison with the results of Mendeléeff. The critical solution temperature was followed closely.

TABLE XVI

Results of Experiment XIII

	Volume	$D\frac{15°}{4°}$	Critical solution temperature
	cc		°C
Original	2050		17.95
Fraction:			
1	20		17.95
2	120	0.793619	17.83
3	250		17.82
4	120	.793608	17.82
5	130		17.82
6	150	.793614	17.85
7	250		17.85
8	250	.793615	17.78
9	50		17.75

Fraction 4 near the middle of the distillate shows the lowest density. The critical solution temperature showed a small decrease as the distillation proceeded and indicated a decreasing water content on the assumption of the absence of other impurities. The differences are hardly significant and the results show a satisfactory agreement with the other experiments. The density of absolute alcohol at 15° is somewhat higher than the corrected result of Mendeléeff.

Experiment XIV.—Fractions from the various distillations (V, 2; IX, 2, 6, C; XIII, 2, 4, 8, 9) were combined and treated with lime as given under Experiment XIII. The same distilling apparatus was also used. Density determinations were made at 15° and 25°.

TABLE XVII

Results of Experiment XIV

Sample	$D\frac{15°}{4°}$	$D\frac{25°}{4°}$	Critical solution temperature
Fraction:			°C
1			17.10
2			17.10
3	0.793596	0.785049	17.10
4	.793595	.785058	17.05
5			17.05
6			

Judging from the results obtained in the determination of the critical solution temperature, there is practically no separation of the alcohol into fractions of different physical properties. The densities obtained are slightly below the mean values obtained in the previous experiments. It is interesting to compare the expansion of fractions 3 and 4 between 15° and 25° with the value called for by the formula obtained in part 2. Here the value for $D^{15°}_{4°} - D^{25°}_{4°}$ is found to be 0.008547 for fraction 3 and 0.008537 for fraction 4, while the formula difference is 0.00854.

7. EFFECT OF IMPURITIES ON THE DENSITY

A study was then made of the effect of small concentrations of possible impurities on the density of anhydrous alcohol and on the critical solution temperature with kerosene mixtures. The effect of acetaldehyde and ethyl ether was studied. Some data were also obtained on the effect of dissolved air. (See p. 407.)

The lower aldehydes, principally acetaldehyde, are the most persistent impurities in alcohol, notwithstanding their much lower boiling points. While tests showed that acetaldehyde was not present in amounts sufficient to affect the density appreciably, yet it was deemed worth while to determine the direction and amount of this effect. Acetaldehyde was made by oxidizing alcohol with chromic-sulphuric acid mixture, then purified and dehydrated by distilling twice from anhydrous calcium chloride. Immediately before making the mixtures the vapor was passed over calcium chloride before condensation. The mixtures were made up by weighing directly. Table XVIII shows the results obtained.

TABLE XVIII

Effect of Acetaldehyde on Density

Mixture	Acetaldehyde	$D^{25°}_{4°}$	Increase in density
	Per cent		
Anhydrous alcohol XII$_3$	0.00	0.785101	0.000000
1	.023	.785144	.000043
2	.140	.785394	.000293
3	.466	.786030	.000929

The aldehyde in mixture 2 could be plainly recognized by odor. Mixture 1 diluted with alcohol to 10 times its volume still gave a strong test for aldehyde by means of the sulphite-fuchsine reaction. Ramsay [338] found 0.7771 to be the density of acetaldehyde at 21°, this temperature being its boiling point. Small variations of the density of the fractions in certain experiments may be due to small quantities of aldehyde. It may be interesting to note the concordance in the various fractions of Experiment XII where aluminum amalgam was used as dehydrating agent and might act as a reducing agent converting the aldehyde into alcohol. One per cent aldehyde lowers the critical solution temperature 0°.5.

Very small quantities of ether are not open to detection by chemical means because of its resistivity toward chemical reagents in general. One would expect the bulk of any ether present to collect in the first fraction on distillation and to be recognizable either by odor or its effect on the density or other physical properties. A few mixtures of known ether content were made up and their density determined. The ether was purified by shaking with dilute sodium hydroxide solution and then washed thoroughly with water to remove the alcohol. After several days' drying over anhydrous calcium chloride it was distilled from sodium wire immediately before use. The mixtures were made up by direct weighing.

TABLE XIX

Effect of Ethyl Ether on Density

Mixture	Ether	$D\frac{25°}{4°}$	Change in density
	Per cent		
Anhydrous alcohol, IV_5..............	0.00	0.785091	....
1	.060	.785070	−0.000021
2	.185	.785019	− .000072

For small amounts of ether in alcohol the results show that 0.1 per cent lowers the density 0.00004. Both mixtures on standing gave a strong odor of ether. Young [566] suggests the possibility that the low density results obtained by Messrs. Squibb [433] may be due to the presence of ether. Assuming the same rate of decrease to hold and taking 0.78506 as the correct value for the density of anhydrous alcohol at 25°, it would take approximately 0.9 per cent ethyl ether to give their low value. This amount could hardly escape detection. One per cent ether lowers the critical solution temperature 2°1.

8. DISCUSSION OF RESULTS

The distillates obtained in Experiments IV and XII answer all the requirements as to purity, judged by the constancy of the physical property determined. That they were not mixtures showing constant physical properties is indicated from the fact that the density results agreed even when different dehydrating agents were used. That the density of the distillate remained essentially unaltered when the distillation was carried on under reduced pressure is additional evidence on this point.

Concerning the freedom from impurities other than water in the distillates showing densities, at 25°, of 0.78506±0.00001, the following is to be said: (1) The fact that fractions of the same density were obtained from samples of different origin points to either a removal of all the significant amounts of impurities or a retention of these impurities in fixed amounts even though using different methods of purification; (2) the good agreement found in the density of the mixtures made up from the distillates and mixtures of distillates with densities showing water content from 0.01 to 0.05 per cent, and from different alcohols, indicates a uniformity in the alcohol characteristic of a pure substance within our present methods of determination.

III. SUMMARY OF RESULTS

1. No difficulty was experienced in obtaining alcohol containing only one-tenth of .1 per cent of water by dehydrating with lime. The dehydration proceeded more rapidly at the boiling temperature of the alcohol. The bulk of the impurities other than water were removed by the rejection of the first and last tenths of the distillate in the preliminary distillation.

2. Chemical methods for removing the last traces of the lower aldehydes were found to be unsatisfactory. This was accomplished by the method of Paul.[77a] Results indicated that minute quan-

tities of aldehydes are produced during the procedure of dehydration and distillation. These quantities can just be detected chemically and were so small as to have no measurable effect on the physical constants determined.

3. An alcohol was obtained which on a further dehydration was not lowered in density and on distillation gave fractions showing the same density within the experimental errors of the determination. Practically the same density value, 0.78506 at 25°, was obtained by using calcium oxide and activated aluminum, and this value is only slightly lower than the results of the more careful previous experimenters. The two dehydrating agents mentioned were equally satisfactory in removing the last traces of water. Slightly higher density values were obtained when calcium was used.

4. By a repetition of Mendeléeff's [307, 341] procedure used in dehydrating alcohol a distillate showing about the same density value was obtained. The various fractions of the distillate showed greater uniformity in density than in his work. A repetition of the work of Messrs. Squibb in its essential details failed to produce alcohol showing the same low density values obtained by them.

5. Small amounts of acetaldehyde increased, while small amounts of ether decreased the density of ethyl alcohol. It was shown that Squibb's [433] low density values can not be ascribed to the presence of ethyl ether.

6. In substantiation of the work of Crismer [1033] and Andrews [1167] the value of the critical solution temperature as a method for detecting small amounts of water in alcohol was demonstrated and shown to have approximately the same sensitiveness as density determinations to one unit in the fifth decimal place.

PART 2

THERMAL EXPANSION OF MIXTURES OF ETHYL ALCOHOL AND WATER

By N. S. Osborne

Part 2 consists of the determination of the thermal expansion between 10° C and 40° C of 12 mixtures of alcohol and water, and the derivation of the coefficients for calculating, between these limits of temperature, the density of any mixture of alcohol and water.

IV. DESCRIPTION OF EXPERIMENTAL WORK

1. METHOD OF DETERMINATION AND GENERAL DESCRIPTION OF APPARATUS

Twelve mixtures whose thermal expansions were investigated were made of approximately integral percentages for convenience, and the concentrations chosen were such as would facilitate interpolation of results. The density of each mixture was twice determined at each of the following temperatures: 10°, 15°, 20°, 25°, 30°, 35°, and 40° C, one series starting with the lower and one with the higher temperature. The density determinations were made by the hydrostatic weighing method—that is, by weighing in the liquid a sinker of known mass and volume.

The arrangement of apparatus is shown in Figs. 5, 6, 7, and 8. The densimeter tube containing the liquid under investigation and the immersed sinker *E* is shown in Fig. 5. A special cap was used for closing the densimeter tube when weighings were not being made. This cap consists of a brass cover "a," fitted to the tube by a soft rubber bushing. Through the center of the cover is a hole, which may be closed by a tightly fitting brass plug. To the upper and lower faces of this plug is attached the suspension wire. The arrangement is shown in Fig. 5. When weighings are in progress, the suspension is as shown at the right, access of the outer air being only through the hole in the cap. When not

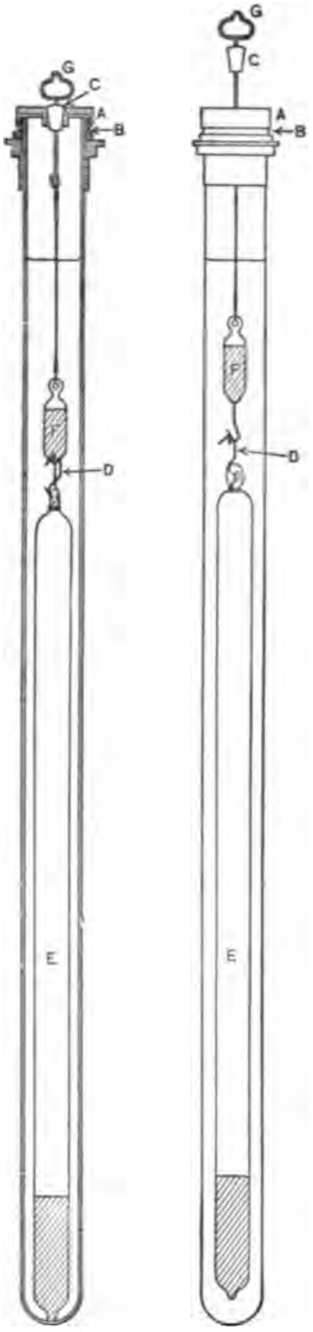


Fig. 5.—*Densimeter tube (one-third size)*

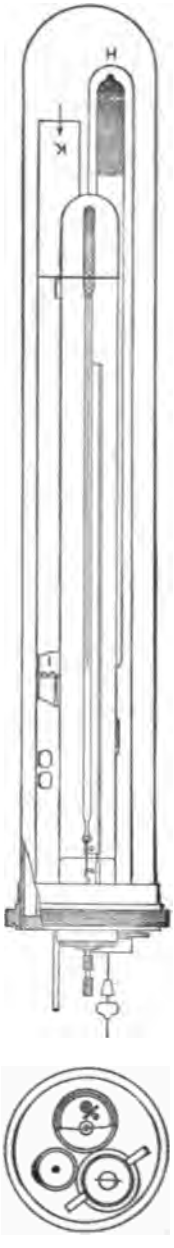


Fig. 6 (*one-fourth size*)

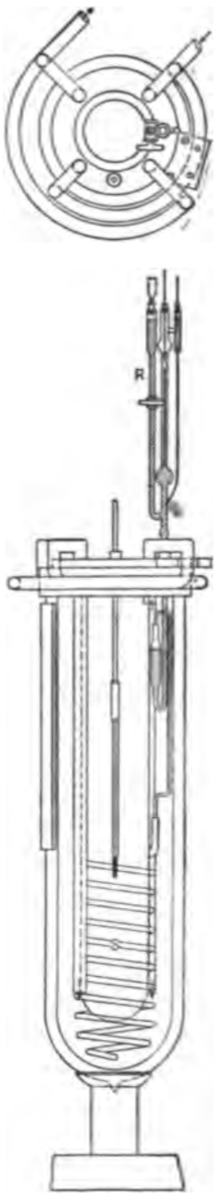


Fig. 8 (*one-eighth size*)

observing, this hole is closed by the plug, as shown at the left, in order to avoid unnecessary changes in concentration of the liquid, caused by evaporation of the alcohol or by absorption of water vapor from the air. In Figs. 6 and 7 the densimeter tube *H* is shown fixed in place in the inner water bath.

The water in the inner bath is kept in constant circulation by the propeller *I*. This bath is immersed in an outer bath kept in constant circulation by means of a motor-driven turbine *N* placed outside the bath. The temperature of this outer bath is maintained constant or changed at will by means of the electric heating coil *O* surrounding the return pipe and by the tubular coil *P* connected with the refrigerating brine supply maintained at a temperature below 0° C. The flow of brine in this coil is adjusted by means of a valve, not shown. The flow of water in the circulating apparatus may, by means of the special valve *Q*, be directed entirely through the cooling chamber, directly through the circulating turbine, or divided, part going either way at will, thus regulating the quantity of heat removed from the system by the brine. The cooling is made slightly in excess of the heat acquired from the surrounding air and that produced by the circulation, the balance being maintained by means of the heating coil.

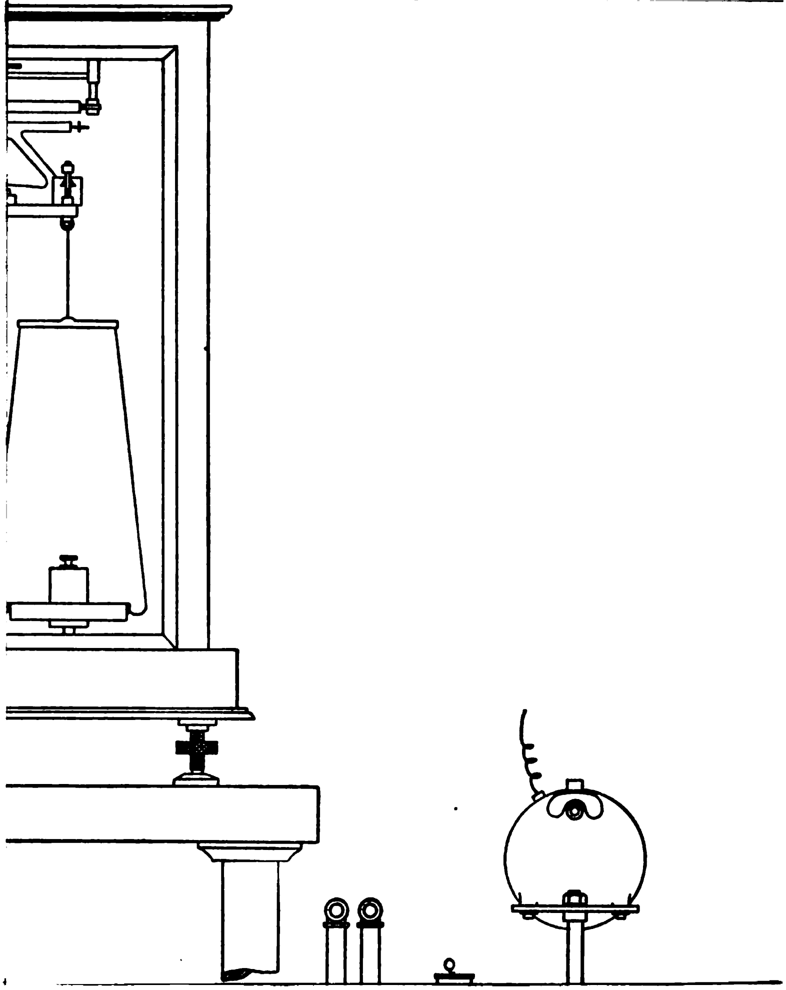
This coil, which has a resistance of 10 ohms, is made of "advance" ribbon, wound over mica on the brass tube through which the return flow takes place. It is used both for regulation of temperature and for rapid heating when changing the temperature. For regulation it is connected in series with a variable resistance composed of a sliding contact wire rheostat and a bank of parallel connected lamps. As a shunt on this variable resistance is connected another lamp bank in the circuit of which is a relay operated by the thermo regulator *R*. The bulb of this thermo regulator is the tubular copper coil *S*, containing about 40 cc of xylol.

A rise in temperature closes an electric circuit, the relay is thus energized, the shunt circuit broken, and the current in the heating coil diminished. When the temperature falls sufficiently, this action is reversed. The sensibility of the regulation varies according to the conditions. Under the most adverse conditions the regulating energy used in the heating coil was from 100 watts to 140 watts and maintained the outer bath constant within 0°.05 C. Under the best conditions the energy varied from 10 to 20 watts, keeping the temperature of the bath constant within 0°.01 C. The periodic variation in temperature of the outer bath was in either case far too rapid to produce any perceptible change in the inner bath. For rapid heating when changing the temperature in the ascending series, the small regulating current was replaced, using a double-throw switch, by a heavy current supplying about 1500 watts in the heating coil.

The outer bath as first arranged is shown in Fig. 7. It is contained in a rectangular tank with plate-glass walls and brass bottom and top. The insulation consisted of two layers of heavy cardboard with cotton between. The water enters at *T* and leaves at *U*, thus insuring complete circulation. Owing to the repeated difficulty on account of leakage of the joints, this tank was replaced by a double-walled glass cylindrical vacuum jacket as shown in Fig. 8. The top was closed by a brass cap cemented to the glass. The water entered by two tubes extending to the bottom and left by two tubes at the top. The greatest difficulty, with this container for the outer bath was the distortion of the image of the thermometers, owing to the cylindrical surface. This was remedied by cementing a plane glass plate to the outside surface, forming a cell which when filled with water corrected most of the aberration. To exclude radiation the cylinder was covered with nickel paper. This vacuum jacket was used principally for the determinations of density of the mixtures of known proportions at constant temperature and was employed for the thermal expansion of only one mixture, 5 III.

The temperatures were observed on two mercury thermometers suspended in water in a tube placed in a position in the inner bath symmetrical to that of the densimeter tube. On Fig. 8 only the upper part of this tube is shown. The holders for the thermometers permitted their rotation and also allowed either of the two to be brought into position for reading. They were read by means of a microscope of long focus which could be moved vertically by means of a rack and pinion.

The reason for placing the thermometers in a tube of water instead of directly in contact with the inner bath was to minimize



the error from temperature lag when bringing the temperature to constancy before observing. The containing tube was slightly larger and thicker walled than the densimeter tube; hence when the thermometers indicated a constant temperature it could be assumed that the liquid in the densimeter tube was at the same constant temperature. In the observations for thermal expansion economy of time did not permit an absolutely constant temperature to be attained, but the observed variation during a density observation extending over about six minutes never exceeded 0°.02 and, with but few exceptions, was always rising. Thus the relative error due to lag in the temperatures of the determinations was small, probably less than 0°.01 except in few instances, and may be regarded as accidental and eliminated in the adjusted results. Examinations of the residuals obtained justifies this assumption.

2. THERMOMETERS USED

Five thermometers were used in this work; they are described in Table XX.

TABLE XX

Thermometer No.	Maker	Date of manufacture	Kind of glass	Range of scale	Length of 1°	Construction
					mm	
4653	Tonnelot	1888	Verre durre	−2°.9 C to +40°.5 C	6.3	Solid, clear stem
2040	Haak	1906	Jena 16^{III}	−1 to +1°C +10 to +31°C	4.8	Inclosed, white scale
264	Richter	1902	do	−0.4 to +0°.4 C +31.5 to +44° C	8.0	Do.
2499	Green	1907	do	−0.5 to +0°.5 C +9 to +31°.5 C	7.5	Solid, white back stem
15938	Baudin	1903	Verre durre	+31.5 to +32°.5 F +89.1 to +115°.6 F	7.2	Do.
15940	do	1903	do	+31.5 to +32.°5 F +88.9 to +115°.8 F	7.2	Do.

All the thermometers were subdivided in tenth-degree divisions. No. 4653 was repaired in 1909 and the bulb reannealed. This thermometer was used in all of the experimental work at every temperature. Nos. 15938 and 15940 were used only for the thermal expansion of 5 III at 35° and 40° C. For this same mixture No. 2499 was used at 10°, 15°, 20°, 25°, and 30° C. For the thermal expansion of all the other mixtures No. 2040 was used at 10°, 15°, 20°, 25°, and 30° C, and No. 264 was used at 35° and 40° C. Every temperature was observed on two thermometers, one always being No. 4653.

The thermometers were calibrated at the points 10°, 15°, 20°, 25°, 30°, 35°, and 40° C by comparison with the primary mercurial standards of the bureau. In the use of the thermometers their ice points were observed after the determination at each temperature, and the corrections to be applied to the observed temperature were deduced from the ice point reading and the calibration corrections. The corrected temperatures are in accordance with the international hydrogen scale.

3. DESCRIPTION OF SINKER

The sinker used in all hydrostatic weighings in this article is designated No. 7. It is made of Jena 16 $^{\text{III}}$ glass. The length over all is 33 cm; the outside diameter is 13 mm. The platinum hook *D*, weighing 0.5327 g, while not permanently sealed to the ring, is considered as a part of the sinker as regards mass and volume. This sinker, which is ballasted with mercury, was made in May, 1908, and was annealed at 450° C before sealing.

The mass as determined at intervals during the progress of the work is given in Table XXI.

TABLE XXI

Determinations of Mass of Sinker No. 7

	Observed mass (grams)
October 22, 1909	99.9991
Do	99.9991
Do	99.9990
Do	99.9990
March 19, 1910	99.9994
Do	99.9987
Do	99.9990
Do	99.9989
Do	99.9988
Do	99.9989
June 16, 1910	99.9991
Do	99.9986
Do	99.9991
Do	99.9989
Mean	99.9990

The volume of the sinker was determined by weighing in distilled water from which the air had been removed. Table XXII gives the determinations of volume made previous to the use of sinker. The results are based on the value of Chappuis [1132] for the expansion of water, using 99.9990 g for the mass of the sinker.

TABLE XXII

Determinations of Volume and Thermal Expansion of Sinker No. 7

Date	Observed mean temperature	Observed mean volume	Reduction to integral temperature		Calculated	Observations
			t	V_t	V_t	
1909		ml		ml	ml	
Oct. 22	3. 93	47. 6958	4	47. 6957	47. 6956	8
Oct. 21	10. 247	47. 7024	10	47. 7019	47. 7020	8
Do	20. 136	47. 7131	20	47. 7128	47. 7128	8
Do	30. 080	47. 7242	30	47. 7239	47. 7238	8
Do	39. 884	47. 7349	40	47. 7348	47. 7350	8
Oct. 22	40. 022	47. 7355	40	47. 7353	47. 7350	8
			25	....	47. 7183	Calculated

Equation for calculation of volume at any temperature:

$$V_t = 47.7172 + [1100.1 \cdot (t-24) + 0.9734 \cdot (t-24)^2] \times 10^{-6}$$

The volume at 25° C was again determined June 10, 1910, and the value found to be 47.7186 ml. For determinations of density where the absolute value is sought, as in part 3 of this work, the mean value for this period, i. e., 47.71844 ml at 25° C is chosen.

4. BALANCE, WEIGHTS, AND METHOD OF WEIGHING

The balance used was a Rueprecht analytical balance of 200 g capacity, provided with special mechanism for rapid weighing and with the outside control of the weights of less than 1 g. The sensibility when undamped was 0.16 mg per division. The weights from 500 mg to 10 mg were the special weights belonging to the balance. The other weights used comprised a set of platinum-plated brass weights from 200 g to 1 g designated as B. S. No. 5157.

Previous to the experimental work the weights were carefully adjusted. A calibration made April, 1909, showed that the error of any possible combination did not exceed +0.08 mg.

A retest made June, 1910, after the completion of the investigation showed the maximum error of any combination to be +0.23 mg. This change is greater than was anticipated, yet is sufficiently small to be disregarded.

The weighings of the sinker in the liquid were made by the method of substitution. A constant counterpoise was kept on the left pan of the balance, while the known weights were applied on the right, from which the sinker was suspended. Equilibrium was first obtained with the immersed sinker attached, then the sinker was detached and left resting on the bottom of the tube while equilibrium was again obtained with the suspending hook alone. The difference in the weights required to secure equilibrium is the apparent weight of the sinker in the liquid.

The suspension wire where it passed through the surface of the liquid was of platinum 0.3 mm in diameter. It was covered with a layer of dull gold by electrodeposition in order to insure wetting with the liquid, and thus avoid the sticking otherwise produced. With the wire thus prepared, weighings could be made to 0.1 mg when the sinker was not attached and to about 0.3 mg with the sinker attached. Since the accidental error of weighing is subject to elimination in the final reduction, weighings to 0.5 mg were accepted as being comparable with the precision in other elements of the work.

All weighings were reduced to vacuo by means of a buoyancy balance, which was devised for obtaining the buoyancy correction to weighings of water for volumetric determinations. This apparatus consists of a hollow bulb of glass having an external volume of 900 cc, suspended from one arm of a balance and counterpoised by a brass weight of equal mass. The weight of air equal in volume to the difference in volume of these two objects is indicated by the weights required on the bulb side to secure a balance. The difference in volume is 881.3 cc; thus the buoyancy on 1 liter of water weighed with brass weights is obtained directly. The air density is obtained by multiplying this observed "buoyancy constant" by $\frac{1}{881.3}$. The bulb is suspended in a glass case to protect it from disturbing air currents. Correction is made for difference in temperature between this case and the balance where the determinations are made. The density of the weights for the purpose of correcting for displaced air is assumed to be 8.4.

5. MATERIAL USED

The water used in the preparation of the mixtures investigated was twice distilled, the second distillation being from alkaline potassium permanganate. The three samples of alcohol used were all prepared from sample A, previously described. The densities at $_{4^\circ}$C and corresponding percentages of alcohol are given below:

Sample	$D\frac{25^\circ}{4^\circ}$C	Per cent alcohol by weight
L_2	0. 78529	99. 93
3 b	. 78533	99. 91
I_3	. 78507	100. 00

Tests made by the chemical division of the bureau failed to show the presence of impurities other than water in sufficient amounts to affect the density appreciably, and it may be safely assumed that the effect on the thermal expansion of these last traces of impurities is less than the experimental error of the determinations.

6. ARRANGEMENT OF EXPERIMENTAL WORK

In order to make the final results of the determination of the thermal expansion as free as possible from the effects of progressive changes in density that are not directly attributable to changes in temperature, the observations were arranged in two series, with the order of the temperatures reversed, the temperatures of density determinations being as follows:

First series	10	15	20	25	30	35	40
Second series	40	35	30	25	20	15	10

In each series the observations were distributed at approximately equal time intervals. Each series required a day for completion.

By employing this isochronously symmetrical arrangement of observations and by taking the mean of the two series disturbing causes which are linear functions of time are practically eliminated.

The principal disturbing causes which were anticipated were evaporation of alcohol and absorption of air and moisture.

Notwithstanding the precautions for the exclusion of atmospheric moisture and prevention of evaporation from the densimeter tube when not actually observing, the change in concentration due to these causes was found to be appreciable in most of the mixtures. Owing to the lower vapor pressure of alcohol the vapor usually is of higher concentration than the mixture which yields it, and thus a progressive dilution of the mixture is produced in most cases. That this dilution is uniformly distributed throughout the mixture is unlikely. There is besides, with some of the mixtures, condensation of the vapor in the top of the tube and on the suspension, which tends to run back into the upper layers of the liquid. This may account for the fact that in the 90 per cent mixture there appeared to be between the series an increase in concentration. The increase in the concentration of the [illegible]0 per cent mixture, however, was artificial, being caused by the intentional addition of alcohol to compensate for evaporation.

It was found that unless dissolved air was extracted from the mixtures there was danger of air being expelled from the liquid at the higher temperatures and attaching to the sinker as bubbles, preventing a successful series of observations. Hence, before the determination for any mixture, and in some cases between the two series of observations, the mixture was evacuated to low pressure to remove a sufficient amount of the dissolved air to prevent this difficulty. During the series air was doubtless reabsorbed and at an unknown rate, but determinations made elsewhere of the effect of dissolved air on the density of various mixtures at 25° C showed the total effect at that temperature to be so small that any large variable effect at the temperatures employed and in the time allowed would be improbable.

Examination of the experimental results shows that the alteration in concentration of the mixtures was usually less for the higher than for the lower per cents of alcohol. It is also seen that between the first and second series of observations on several of the mixtures a considerable change occurred. This can be attributed to the evacuation of the mixture previous to the second series to remove air by which alcohol vapor was also removed.

The manner of observing was as follows: With the liquid to be investigated in the tube, the sinker immersed, the cap on and closed by the suspension plug, and the tube in place in the control bath, the temperature was brought to the initial temperature of the series. The brine flow, the by-pass in the circulating apparatus, the thermoregulator, and the electric energy supply were successively adjusted to maintain the desired constant temperature. Sufficient time was allowed for the inner bath to acquire a constant or very slowly rising temperature. The sinker was then suspended from the balance and weighed. The thermometers were both read. The sinker was detached and the suspension weighed. The sinker was again suspended and weighed and the thermometers again read. At the conclusion of this set of observations the top of the densimeter tube was closed by the suspension plug and the temperature changed to the next one of the series as rapidly as the capacity of the heating coil or of the cooling coil would permit. While this temperature change was taking place the ice points of the thermometers were read and the buoyancy constant observed. The temperature control was readjusted for constant regulation at the new temperature and observations for density and temperature were again made. This procedure was repeated until the series was complete.

V. EXPERIMENTAL RESULTS

1. CALCULATION OF RESULTS

The total correction to the thermometer at the temperature of the determination was obtained by use of the observed ice points and the calibration corrections. Each observed temperature was corrected and the mean of the set of four taken as the temperature of the determination.

The apparent weight of the sinker in the liquid is given by the difference between the balance readings with sinker on and with sinker off. The mean of the two values of the apparent weight of sinker thus obtained is corrected by subtracting the weight of air displaced by the weights. To obtain this correction the volume of the weights (assuming their density to be 8.4) is multiplied by the observed air density. The application of this correction gives the true weight of the sinker in the liquid. The difference between

TABLE XXIII

Determination of Thermal Expansion of Alcohol-Water Mixture Containing 49.961 Per Cent Alcohol

Record of Observations and Calculations

SERIES 1.—JAN. 28, 1910. RECORD: VOL. 646, p. 122. OBSERVERS: N. S. O., H. W. B.

Time	Observed temperature		Observed ice point and *Total correction*		Corrected temperature		Mean temperature of set t'	Balance reading (a) Sinker on (b) *Sinker off* (c) Sinker on	Apparent weight of sinker in liquid	Buoyancy correction on weights	True weight of sinker in liquid	Weight of displaced liquid	Volume of sinker at t°	Density at observed temperature $D\frac{'t}{4}$
	Haak No. 2040	Tonnelot No. 4653	Haak No. 2040	Tonnelot No. 4653	Haak No. 2040	Tonnelot No. 4653		g	g	g	g	g	ml	
a. m. 11.07	10.020	9.925	+0.088	−0.100	10.019	10.016		39.2972	56.0427					
11.12							10.019	*95.3399*		−0.0078	56.0349	43.9643	47.70221	0.921641
11.14	10.025	9.927	*−0.001*	*+0.091*	10.024	10.018		39.2972	56.0427					
p. m. 12.14	15.020	14.940	+0.085	−0.102	15.012	15.005		39.1120	56.2213					
12.18							15.011	*95.3333*		−0.0078	56.2136	43.7856	47.70759	0.917791
12.21	15.025	14.945	*−0.008*	*+0.065*	15.017	15.010		39.1118	56.2215					
1.16	19.995	19.945	+0.082	−0.110	20.000	19.986		38.9238	56.4027					
1.19							19.993	*95.3265*		−0.0079	56.3949	43.6043	47.71301	0.913887
1.24	19.990	19.950	*+0.005*	*+0.041*	19.995	19.991		38.9236	56.4029					
2.05	25.015	24.980	+0.080	−0.115	25.005	25.003		38.7314	56.5882					
2.07							25.006	*95.3196*		−0.0079	56.5804	43.4188	47.71851	0.909894
2.11	25.020	24.985	*−0.010*	*+0.023*	25.010	25.008		38.7312	56.5884					
2.49	29.980	29.970	+0.075	−0.118	29.985	29.983		38.5371	56.7757					
2.54							29.986	*95.3128*		−0.0079	56.7678	43.2314	47.72408	0.905862
2.57	29.985	29.973	*+0.005*	*+0.013*	29.990	29.986		38.5371	56.7757					
	Richter No. 264		Richter No. 264		Richter No. 264									
3.30	34.987	34.925	+0.027	−0.120	34.950	34.960		38.3404	56.9652					
3.33							34.959	*95.3056*		−0.0079	56.9571	43.0421	47.72958	0.901791
3.38	34.998	34.930	*−0.037*	*+0.035*	34.961	34.965		38.3407	56.9649					
4.13	39.990	39.880	+0.025	−0.125	39.957	39.958		38.1386	57.1597					
4.17							39.959	*95.2983*		−0.0080	57.1517	42.8475	47.73521	0.897608
4.20	39.995	39.880	*−0.033*	*+0.078*	39.962	39.958		38.1386	57.1597					

Air temperature: In balance, 21°.5; at buoyancy bulb, 19°.6. Buoyancy constant: Observed, 1040; corrected, 1032. Air density, 0.001172 g/cm³. Weight of sinker, 99.9990 g.

SERIES 2.—JAN. 29, 1910. RECORD VOL. 646, P. 122

a. m.	Richter No. 264	Tonnelot No. 4653	Richter No. 264	Ton nelot No. 4653	Richter No. 264	Tonnelot No. 4653		g	g	g	g	g	ml	
10.18	39.988	39.880	+0.025	−0.125	39.955	39.958		38.1406	57.1581					
10.22							39.954	*95.2987*		−0.0079	57.1501	42.8491	47.73519	0.897642
10.26	39.985	39.875	*−0.035*	*+0.078*	39.952	39.953		38.1408	57.1579					
10.57	35.015	34.950	+0.025	−0.123	34.980	34.988		38.3422	56.9636					
11.01							34.986	*95.3058*		−0.0079	56.9556	43.0436	47.72961	0.901822
11.05	35.022	34.950	*−0.085*	*+0.058*	34.987	34.988		38.3424	56.9634					
	Haak No. 2040		Haak No. 2040		Haak No. 2040									
11.39	29.995	29.977	+0.075	−0.120	30.000	29.992		38.5395	56.7734					
11.43							29.998	*95.3129*		−0.0078	56.7654	43.2338	47.72404	0.905912
11.49	30.080	29.980	*+0.006*	*+0.016*	30.005	29.995		38.5400	56.7729					
p. m.														
12.19	25.025	24.990	+0.080	−0.120	25.015	25.018		38.7348	56.5848					
12.23							25.015	*95.3198*		−0.0078	56.5770	43.4222	47.71852	0.909965
12.25	25.025	24.985	*−0.010*	*+0.088*	25.015	25.013		38.7348	56.5848					
1.19	19.995	19.955	+0.080	−0.115	20.002	20.001		38.9274	56.3991					
1.22							20.003	*95.3365*		−0.0078	56.3913	43.6079	47.71302	0.913962
1.25	20.000	19.955	*+0.007*	*+0.046*	20.007	20.001		38.9274	56.3991					
2.07	15.020	14.940	+0.082	−0.112	15.015	15.015		39.1162	56.2170					
2.10							15.014	*95.3338*		−0.0078	56.2092	43.7900	47.70759	0.917883
2.12	15.020	14.935	*−0.006*	*+0.076*	15.015	15.010		39.1162	56.2170					
2.56	10.020	9.925	+0.088	−0.108	10.019	10.024		39.3018	56.0380					
3.00							10.020	*95.3398*		−0.0078	56.0302	43.9690	47.70221	0.921739
3.02	10.020	9.920	*−0.001*	*+0.099*	10.019	10.019		39.3018	56.0380					

Air temperature: In balance, 21°.2; at buoyancy bulb, 19°.2. Buoyancy constant: Observed, 1028; corrected, 1020. Air density, 0.001158.

the weight of the sinker in the liquid and its weight in vacuo gives the weight of the liquid displaced by the sinker. This weight divided by the volume of the sinker at the temperature of the determination gives the density of the liquid at that temperature in grams per milliliter.

The calculation of the density of the liquid as described above may be expressed by the following equation:

$$D_{\frac{t}{4}} = \frac{S - \frac{W_1 - w + W_2 - w}{2}\left(1 - \frac{\rho}{8.4}\right)}{V_t}$$

Where $D_{\frac{t}{4}}$ = density of sample at temperature t

S = mass of sinker

V_t = volume of sinker at the temperature t

t = temperature of determination

W_1, W_2 = balance readings with sinker on

w = balance readings with sinker off

ρ = air density

2. COPY OF ORIGINAL DATA

A copy of the record showing the observations comprising the two series of determinations for a single mixture is given in Table XXIII (pp. 382–383). This table illustrates the arrangement of the experimental work and also the calculation of results as described above.

3. REDUCTION AND ADJUSTMENT OF RESULTS

From the observations and calculations as described and illustrated above are obtained the experimental results given in Tables XXIV to XXXV, comprising for each mixture a double series of density determinations together with the corresponding temperatures. These temperatures are all very close to the integral temperatures intended. For the purpose of simplifying the adjustment of results the determined densities are reduced to the values corresponding to the integral temperatures. Comparison between the densities thus reduced shows the permanent change occurring in the liquid during the progress of the determination not directly attributable to the change in temperature. This permanent change which is caused by the evaporation of alcohol and by the abosrption of moisture may be regarded as a linear function of the position of the determination in the series, since the different groups of observations in a series occupy approximately the same time and are separated by equal intervals of time. The total permanent change occurring between any determination of the first series and the corresponding one of the second is represented by the equation:

$$\varDelta = a + b\ (7 - n)$$

where n is the number of the determination in the first series, a is the change occurring between the first and second series—that is, between the seventh and eighth determinations—and may include changes from any intentional or accidental cause, b depends on the rate of change during the progress of a single series and is assumed to be the same in the two series. By a least square adjustment of the observed apparent permanent change in density between the series, the constants a and b are determined. The adjusted value of $\varDelta$ is then calculated by these coefficients, and each determined density corrected by one-half the corresponding adjusted $\varDelta$ with the appropriate sign.

It is evident that the final value of the density at each temperature will be the same whether the mean be taken of the two determinations at that temperature or whether these determinations be first adjusted, as indicated above, to correct for the progressive change of density due to evaporation of alcohol and absorption of water vapor. This adjustment, however, is desirable in order that a check may be had upon the agreement of the two determinations when all explainable differences have been taken into account. This agreement is an indication of the magnitude of the accidental errors of the individual determinations.

The observed densities thus adjusted to values corresponding to the mean concentration of the mixture are further adjusted on the assumption that the equation

$$D_{4}^{t} = D_{4}^{25} + \alpha\ (t-25) + \beta\ (t-25)^2 + \gamma\ (t-25)^3$$

represents the change in density depending on the change in temperature alone. By the method of least squares, D_{4}^{25}, α, β, γ are determined. The adjusted value of D_{4}^{t} is then calculated. In the values of observed D_{4}^{t} minus calculated D_{4}^{t} will be combined the accidental experimental errors as well as errors due to the assumed form of functions in the least square adjustments of the observations. It appears from examination of these residuals that the assumptions made are in accordance with the experimental data, unless these errors are systematically compensated, as the residuals are seen to be within the limits of accidental error.

TABLE XXIV

Determination of Thermal Expansion of Alcohol-Water Mixture Containing 4.907 Per Cent Alcohol by Weight

Reduction and Adjustment of Experimental Results

Determination number	Observed temperature t'	Observed density D'^{t}_{4}	Reduction to integral temperature		Apparent permanent change between series $\Delta \times 10^6$	Adjusted correction for permanent change $\frac{\Delta}{2} \times 10^6$	Density adjusted to mean concentration D^{t}_{4}	Mean observed density D^{t}_{4}	Calculated D^{t}_{4}	Observed D^{t}_{4} minus calculated $D^{t}_{4} \times 10^6$
			t	D''^{t}_{4}						
1	39. 931	0. 983244	40	0. 983216	100	+49	0. 983265	0. 983266	0. 983267	− 2
14	39. 930	. 983344		. 983316		−49	. 983267			0
2	34. 984	. 985125	35	. 985119	96	+48	. 985167	. 985167	. 985163	+ 4
13	34. 963	. 985228		. 985215		−48	. 985167			+ 4
3	30. 021	. 986800	30	. 986807	92	+48	. 986855	. 986853	. 986854	+ 1
12	30. 017	. 986894		. 986899		−48	. 986851			− 3
4	25. 028	. 988262	25	. 988270	84	+47	. 988317	. 988312	. 988317	0
11	25. 042	. 988343		. 988354		−47	. 988307			−10
5	20. 008	. 989478	20	. 989480	107	+46	. 989526	. 989534	. 989530	− 4
10	20. 018	. 989583		. 989587		−46	. 989541			+11
6	15. 018	. 990419	15	. 990422	92	+46	. 990468	. 990468	. 990468	0
9	15. 022	. 990511		. 990514		−46	. 990468			0
7	10. 053	. 991060	10	. 991065	86	+45	. 991110	.991108	.991108	+ 2
8	10. 036	. 991147		. 991151		−45	. 991106			− 2

Equation for adjustment of Δ: $\Delta = 90 + 1.285\ (7-n)$.

Probable value of D^{t}_{4} from above determinations: $D^{t}_{4} = 0.988317 - [268.4\ (t-25) + 5.02\ (t-25)^2 - 0.0311\ (t-25)^3]10^6$.

TABLE XXV

Determination of Thermal Expansion of Alcohol-Water Mixture Containing 9.984 Per Cent of Alcohol by Weight

Reduction and Adjustment of Experimental Results

Determination number	Observed temperature t'	Observed density D'^{t}_{4}	Reduction to integral temperature		Apparent permanent change between series $\Delta' \times 10^6$	Adjusted correction for permanent change $\frac{\Delta}{2} \times 10^6$	Density adjusted to mean concentration D^{t}_{4}	Mean observed density D^{t}_{4}	Calulated D^{t}_{4}	Observed D^{t}_{4} minus calculated $D^{t}_{4} \times 10^6$
			t	D''^{t}_{4}						
1	40. 002	0. 974768	40	0. 974769	22	+ 8	0. 974777	0. 974780	0. 974781	−4
14	39. 966	. 974806		. 974791		−8	. 974783			+2
2	35. 001	. 976880	35	. 976880	11	+6	. 976886	. 976886	. 976884	+2
13	34. 976	. 976901		. 976891		−6	. 976885			+1
3	30. 026	. 978774	30	. 978783	1	+4	. 978787	. 978784	. 978784	+3
12	29. 989	. 978788		. 978784		−4	. 978780			−4
4	25. 016	. 980458	25	. 980463	−5	+2	. 980465	. 980460	. 980461	+4
11	25. 019	. 980452		. 980458		−2	. 980456			−5
5	20. 019	. 981887	20	. 981892	5	0	. 981892	. 981894	. 981896	−4
10	20. 022	. 981891		. 981897		0	. 981897			+1
6	15. 038	. 983063	15	. 983071	5	−2	. 983069	. 983074	. 983070	−1
9	15. 020	. 983072		. 983076		+2	. 983078			+8
7	10. 039	. 983962	10	. 983968	−11	−4	. 983964	. 983962	. 983963	+1
8	10. 048	. 983950		. 983957		+4	. 983961			−2

Equation for adjustment of Δ: $\Delta = -7.5 + 3.822\ (7 - n)$.

Probable value of D^{t}_{4} from above determinations: $D^{t}_{4} = 0.980461 - [0.311.9\ (t-25) + 4.84\ (t-25)^2 - 0.0258\ (t-25)^3]10^{-6}$.

TABLE XXVI

Determination of Thermal Expansion of Alcohol-Water Mixture Containing 19.122 Per Cent Alcohol by Weight

Reduction and Adjustment of Experimental Results

Determination number	Observed temperature t'	Observed density D'^{t}_{4}	Reduction to integral temperature		Apparent permanent change between series $\Delta' \times 10^6$	Adjusted correction for permanent change $\frac{\Delta}{2} \times 10^6$	Density adjusted to mean concentration D^{t}_{4}	Mean observed density D^{t}_{4}	Calculated D^{t}_{4}	Observed D^{t}_{4} minus calculated $D^{t}_{4} \times 10^6$
			t	D''^{t}_{4}						
1	10.052	0.973455	10	0.973472	35	+22	0.973494	0.973490	0.973492	+ 2
14	10.037	.973495		.973507		−22	.973485			− 7
2	15.021	.971736	15	.971744	42	+20	.971764	.971765	.971763	+ 1
13	15.028	.971776		.971786		−20	.971766			+ 3
3	20.025	.969783	20	.969793	37	+19	.969812	.969812	.969810	+ 2
12	20.033	.969816		.969830		−19	.969811			+ 1
4	25.020	.967608	25	.967617	51	+18	.967635	.967642	.967648	−13
11	25.042	.967649		.967668		−18	.967650			+ 2
5	29.992	.965275	30	.965271	37	+17	.965288	.965290	.965289	− 1
10	30.036	.965290		.965308		−17	.965291			+ 2
6	34.990	.962742	35	.962737	26	+16	.962753	.962750	.962747	+ 6
9	34.993	.962767		.962763		−16	.962747			0
7	39.966	.960042	40	.960023	23	+14	.960037	.960034	.960036	+ 1
8	39.966	.960065		.960046		−14	.960032			− 4

Equation for adjustment of Δ: $\Delta = 28.6 + 2.430\ (7 - n)$.

Probable value of D^{t}_{4} from above determinations: $D^{t}_{4} = 0.967648 - [452.6\ (t-25) + 3.93\ (t-25)^2 - 0.0180\ (t-25)^3]\ 10^{-6}$.

TABLE XXVII

Determination of Thermal Expansion of Alcohol-Water Mixture Containing 22.918 Per Cent Alcohol by Weight

Reduction and Adjustment of Experimental Results

Determination number	Observed temperature t'	Observed density D'^{t}_{4}	Reduction to integral temperature		Apparent permanent change between series $\Delta' \times 10^6$	Adjusted correction for permanent change $\frac{\Delta}{2} \times 10^6$	Density adjusted to mean concentration D^{t}_{4}	Mean observed density D^{t}_{4}	Calculated D^{t}_{4}	Observed D^{t}_{4} minus calculated $D^{t}_{4} \times 10^6$
			t	D''^{t}_{4}						
1	10.015	0.969152	10	0.969158	64	+38	0.969196	0.969190	0.969190	+ 6
14	10.021	.969213		.969222		−38	.969184			− 6
2	14.995	.966981	15	.966979	71	+36	.967015	.967014	.967016	− 1
13	15.011	.967045		.967050		−36	.967014			− 2
3	20.002	.964626	20	.964627	73	+35	.964662	.964664	.964660	+ 2
12	20.011	.964695		.964700		−35	.964665			+ 5
4	24.989	.962097	25	.962091	76	+33	.962124	.962129	.962133	− 9
11	25.019	.962157		.962167		−33	.962134			+ 1
5	29.990	.959408	30	.959402	76	+32	.959434	.959440	.959440	− 6
10	29.998	.959479		.959478		−32	.959446			+ 6
6	34.981	.956568	35	.956557	64	+30	.956587	.956589	.956588	− 1
9	34.980	.956633		.956621		−30	.956591			+ 3
7	39.972	.953583	40	.953566	40	+29	.953595	.953586	.953587	+ 8
8	39.955	.953634		.953606		−29	.953577			−10

Equation for adjustment of Δ: $\Delta = 57.4 + 2.963(7 - n)$.

Probable value of D^{t}_{4} from above determinations: $D^{t}_{4} = 0.962133 - [522.4\ (t-25) + 3.31\ (t-25)^2 - 0.0100\ (t-25)^3]\ 10^{-6}$.

TABLE XXVIII

Determination of Thermal Expansion of Alcohol-Water Mixture Containing 30.086 Per Cent Alcohol, by Weight

Reduction and Adjustment of Experimental Results

Determination number	Observed temperature t'	Observed density $D^{t'}_4$	Reduction to integral temperature		Apparent permanent change between series $\Delta' \times 10^6$	Adjusted correction for permanent change $\frac{\Delta}{2} \times 10^6$	Density adjusted to mean concentration D^t_4	Mean observed density D^t_4	Calculated D^t_4	Observed D^t_4 minus calculated $D^t_4 \times 10^6$
			t	D''^{t}_4						
1	10.024	0.959538	10	0.959552	201	+103	0.959655	0.959652	0.959650	+ 5
14	10.019	.959742		.959753		−103	.959650			0
2	15.001	.956626	15	.956627	194	+102	.956729	.956724	.956729	0
13	15.011	.956814		.956821		−102	.956719			−10
3	20.002	.953589	20	.953590	205	+100	.953690	.953692	.953686	+ 4
12	20.014	.953786		.953795		−100	.953695			+ 9
4	25.011	.950422	25	.950429	199	+ 99	.950528	.950528	.950529	− 1
11	25.022	.950614		.950628		− 99	.950529			0
5	29.986	.947160	30	.947151	216	+ 97	.947248	.947259	.947258	−10
10	30.006	.947363		.947367		− 97	.947270			+12
6	34.964	.943796	35	.943771	206	+ 96	.943867	.943874	.943877	−10
9	34.983	.943989		.943977		− 96	.943881			+ 4
7	39.963	.940335	40	.940309	163	+ 95	.940404	.940390	.940390	+14
8	39.958	.940501		.940472		− 95	.940377			−13

Equation for adjustment of Δ: $\Delta = 189.2 + 2.841(7 - n)$.

Probable value of D^t_4 from above determinations: $D^t_4 = 0.950529 - [643.1(t-25) + 2.26(t-25)^2 - 0.0047(t-25)^3]10^{-6}$.

TABLE XXIX

Determination of Thermal Expansion of Alcohol-Water Mixture Containing 39.988 Per Cent Alcohol, by Weight

Reduction and Adjustment of Experimental Results

Determination number	Observed temperature t'	Observed density $D^{t'}_4$	Reduction to integral temperature		Apparent permanent change between series $\Delta' \times 10^6$	Adjusted correction for permanent change $\frac{\Delta}{2} \times 10^6$	Density adjusted to mean concentration D^t_4	Mean observed density D^t_4	Calculated D^t_4	Observed D^t_4 minus calculated $D^t_4 \times 10^6$
			t	D''^t_4						
1	10.017	0.942340	10	0.942352	126	+68	0.942420	0.942415	0.942415	+5
14	10.035	.942453		.942478		−68	.942410			−5
2	15.014	.938777	15	.938787	128	+65	.938852	.938851	.938851	+1
13	15.020	.938901		.938915		−65	.938850			−1
3	20.007	.935149	20	.935154	130	+63	.935217	.935219	.935215	+2
12	20.018	.935271		.935284		−63	.935221			+6
4	25.012	.931431	25	.931440	124	+60	.931500	.931502	.931507	−7
11	25.020	.931564		.931564		−60	.931504			−3
5	29.984	.927680	30	.927668	118	+57	.927725	.927727	.927727	−2
10	29.997	.927788		.927786		−57	.927729			+2
6	34.998	.923818	35	.923816	119	+55	.923871	.923876	.923874	−3
9	34.982	.923949		.923935		−55	.923880			+6
7	39.946	.919942	40	.919899	95	+52	.919951	.919946	.919947	+4
8	39.969	.920019		.919994		−52	.919942			−5

Equation for adjustment of Δ: $\Delta = 103.6 + 5.464\ (7 - n)$.

Probable value of D^t_4 from above determinations: $D^t_4 = 0.931507 - [748.8(t-25) + 1.45(t-25)^2 + 0.0004(t-25)^3]10^{-6}$.

TABLE XXX

Determination of Thermal Expansion of Alcohol-Water Mixture Containing 49.961 Per Cent Alcohol by Weight

Reduction and Adjustment of Experimental Results

Determination number	Observed temperature t'	Observed density D'^{t}_{4}	Reduction to integral temperature		Apparent permanent change between series $\Delta' \times 10^6$	Adjusted correction for permanent change $\frac{\Delta}{2} \times 10^6$	Density adjusted to mean concentration D^{t}_{4}	Mean observed density D^{t}_{4}	Calculated D^{t}_{4}	Observed D^{t}_{4} minus calculated $D^{t}_{4} \times 10^6$
			t	D''^{t}_{4}						
1	10.019	0.921641	10	0.921655	99	+52	0.921707	0.921704	0.921705	+ 2
14	10.020	.921739		.921754		−52	.921702			− 3
2	15.011	.917791	15	.917800	94	+47	.917847	.917847	.917844	+ 3
13	15.014	.917883		.917894		−47	.917847			+ 3
3	19.993	.913887	20	.913881	83	+41	.913922	.913922	.913922	0
12	20.003	.913962		.913964		−41	.913923			+ 1
4	25.006	.909894	25	.909899	78	+35	.909934	.909938	.909937	− 3
11	25.015	.909965		.909977		−35	.909942			+ 5
5	29.986	.905862	30	.905851	59	+30	.905881	.905880	.905888	− 7
10	29.998	.905912		.905910		−30	.905880			− 8
6	34.959	.901791	35	.901757	53	+24	.901781	.901784	.901774	+ 7
9	34.986	.901822		.901810		−24	.901786			+12
7	39.959	.897608	40	.897573	30	+19	.897592	.897588	.897591	+ 1
8	39.954	.897642		.897603		−19	.897584			− 7

Equation for adjustment of Δ: $\Delta = 37.5 + 11.14(7 - n)$.

Probable value of D^{t}_{4} from above determinations: $D^{t}_{4} = 0.909937 - [803.3(t-25) + 1.28(t-25)^2 + 0.0024(-25)^3]10^{-6}$.

TABLE XXXI

Determination of Thermal Expansion of Alcohol-Water Mixture Containing 59.976 Per Cent Alcohol by Weight

Reduction and Adjustment of Experimental Results

Determination number	Observed temperature t'	Observed density D'^{t}_{4}	Reduction to integral temperature		Apparent permanent change between series $\Delta' \times 10^6$	Adjusted correction for permanent change $\frac{\Delta}{2} \times 10^6$	Density adjusted to mean concentration D^{t}_{4}	Mean observed density D^{t}_{4}	Calculated D^{t}_{4}	Observed D^{t}_{4} minus calculated $D^{t}_{4} \times 10^6$
			t	D''^{t}_{4}						
1	10.023	0.899275	10	0 899293	60	+33	0.899326	0.899323	0.899323	+3
14	10.024	.899334		.899353		−33	.899320			−3
2	14.998	.895260	15	.895258	62	+31	.895289	.895289	.895290	−1
13	15.025	.895300		.895320		−31	.895289			−1
3	20.001	.891172	20	.891173	57	+29	.891202	.891202	.891200	+2
12	20.028	.891230		.891230		−29	.891201			+1
4	25.018	.887002	25	.887017	64	+27	.887044	.887049	.887051	−7
11	25.043	.887045		.887081		−27	.887054			+3
5	29.980	.882832	30	.882815	54	+26	.882841	.882842	.882842	−1
10	29.996	.882872		.882869		−26	.882843			+1
6	34.974	.878566	35	.878544	51	+24	.878568	.878570	.878570	−2
9	34.976	.878616		.878595		−24	.878571			+1
7	39.969	.874243	40	.874216	34	+22	.874238	.874233	.874233	+5
8	39.977	.874220		.874250		−22	.874228			−5

Equation for adjustment of Δ: $\Delta = 43.6 + 3.68(7 - n)$.

Probable value of D^{t}_{4} from above determinations: $D^{t}_{4} = 0.887051 - [835.8(t-25) + 1.21(t-25)^2 + 0.0024(t-25)^3]10^{-6}$.

TABLE XXXII

Determination of Thermal Expansion of Alcohol-Water Mixture Containing 70.012 Per Cent Alcohol by Weight

Reduction and Adjustment of Experimental Results

Determination number	Observed temperature t'	Observed density D'^{t}_{4}	Reduction to integral temperature		Apparent permanent change between series $\Delta' \times 10^6$	Adjusted correction for permanent change $\frac{\Delta}{2} \times 10^6$	Density adjusted to mean concentration D^{t}_{4}	Mean observed density D^{t}_{4}	Calculated D^{t}_{4}	Observed D^{t}_{4} minus calculated $D^{t}_{4} \times 10^6$
			t	D''^{t}_{4}						
1	10.034	0.875938	10	0.875966	46	+21	0.875987	0.875989	0.875989	−2
14	10.018	.875997		.876012		−21	.875991			+2
2	15.014	.871819	15	.871831	34	+20	.871851	.871848	.871845	+6
13	15.023	.871846		.871865		−20	.871845			0
3	20.002	.867621	20	.867623	33	+19	.867642	.867640	.867641	+1
12	20.022	.867637		.867656		−19	.867637			−4
4	25.016	.863344	25	.863358	39	+18	.863376	.863378	.863380	−4
11	25.040	.863363		.863397		−18	.863379			−1
5	29.995	.859045	30	.859041	38	+16	.859057	.859060	.859060	−3
10	30.004	.859076		.859079		−16	.859063			+3
6	34.988	.854675	35	.854664	38	+15	.854679	.854683	.854681	−2
9	34.998	.854704		.854702		−15	.854687			+6
7	39.979	.850250	40	.850231	19	+14	.850245	.850240	.850241	+4
8	39.988	.850261		.850250		−14	.850236			−5

Equation for adjustment of Δ: $\Delta = 28.0 + 2.428\ (7-n)$.

Probable value of D^{t}_{4} from above determinations: $D^{t}_{4} = 0.863380 - [858.1\ (t-25) + 1.17\ (t-25)^2 + 0.0009\ (t-25)^3]\ 10^{-6}$.

TABLE XXXIII

Determination of Thermal Expansion of Alcohol-Water Mixture Containing 80.036 Per Cent Alcohol by Weight

Reduction and Adjustment of Experimental Results

Determination number	Observed temperature t'	Observed density $D^{t'}_4$	Reduction to integral temperature		Apparent permanent change between series $\Delta' \times 10^6$	Adjusted correction for permanent change $\frac{\Delta}{2} \times 10^6$	Density adjusted to mean concentration D^t_4	Mean observed density D^t_4	Calculated D^t_4	Observed D^t_4 minus calculated $D^t_4 \times 10^6$
			t	D'^t_4						
1	10.032	0.851856	10	0.851883	−1	−1	0.851882	0.851882	0.851882	0
14	10.026	.851860		.851882		+1	.851883			+1
2	15.028	.847619	15	.847643	−1	0	.847643	.847642	.847644	−1
13	15.019	.847626		.847642		0	.847642			−2
3	20.025	.843342	20	.843364	−2	+1	.843365	.843363	.843362	+3
12	20.029	.843337		.843362		−1	.843361			−1
4	25.034	.838997	25	.839027	5	+2	.839029	.839030	.839031	−2
11	25.025	.839010		.839032		−2	.839030			−1
5	30.006	.834636	30	.834641	11	+3	.834644	.834646	.834646	−2
10	30.020	.834634		.834652		−3	.834649			+3
6	34.988	.830210	35	.830199	6	+4	.830203	.830202	.830202	+1
9	34 994	.830210		.830205		−4	.830201			−1
7	39.966	.825722	40	.825691	7	+5	.825696	.825694	.825694	+2
8	39.981	.825715		.825698		−5	.825693			−1

Equation for adjustment of Δ: $\Delta = 9.1 - 1.821\ (7-n)$.

Probable value of D^t_4 from above determinations: $D^t_4 = 0.839031 - [871.4\ (t-25) + 1.08\ (t-25)^2 + 0.0069\ (t-25)^3]\ 10^{-6}$.

TABLE XXXIV

Determination of Thermal Expansion of Alcohol-Water Mixture Containing 90.037 Per Cent Alcohol by Weight

Reduction and Adjustment of Experimental Results

Determination number	Observed temperature t'	Observed density D'^{t}_{4}	Reduction to integral temperature		Apparent permanent change between series $\Delta' \times 10^6$	Adjusted correction for permanent change $\frac{\Delta}{2} \times 10^6$	Density adjusted to mean concentration D^{t}_{4}	Mean observed density D^{t}_{4}	Calculated D^{t}_{4}	Observed D^{t}_{4} minus calculated $D^{t}_{4} \times 10^6$
			t	D''^{t}_{4}						
1	10. 029	0. 826431	10	0. 826456	−29	−15	0. 826441	0. 826442	0. 826443	−2
14	10. 034	. 826398		. 826427		+15	. 826442			−1
2	15. 022	. 822169	15	. 822188	−28	−14	. 822174	. 822174	. 822174	0
13	15. 031	. 822133		. 822160		+14	. 822174			0
3	20. 015	. 817862	20	. 817875	−18	−12	. 817863	. 817866	. 817866	−3
12	20. 010	. 817848		. 817857		+12	. 817869			+3
4	25. 012	. 813519	25	. 813529	−28	−11	. 813518	. 813515	. 813516	+2
11	25. 036	. 813470		. 813501		+11	. 813512			−4
5	29. 986	. 809144	30	. 809132	−25	−10	. 809122	. 809120	. 809120	+2
10	30. 009	. 809099		. 809107		+10	. 809117			−3
6	34. 980	. 804698	35	. 804680	−16	− 9	. 804671	. 804672	. 804673	−2
9	34. 996	. 804668		. 804664		+ 9	. 804673			0
7	39. 990	. 800187	40	. 800178	−14	− 8	. 800170	. 800171	. 800172	−2
8	39. 987	. 800176		. 800164		+ 8	. 800172			0

Equation for adjustment of Δ: $\Delta = -16 - 2.213\ (7 - n)$.

Probable value of D^{t}_{4} from above determinations: $D^{t}_{4} = 0.813516 - [874.6\ (t-25) + 0.93\ (t-25)^2 + 0.0051\ (t-25)^3]\ 10^{-6}$.

TABLE XXXV

Determination of Expansion of Alcohol-Water Mixture Containing 99.913 Per Cent Alcohol by Weight

Reduction and Adjustment of Experimental Results

Determination number	Observed temperature t'	Observed density D'^{t}_{4}	Reduction to integral temperature		Apparent permanent change between series $\Delta' \times 10^6$	Adjusted correction for permanent change $\frac{\Delta}{2} \times 10^6$	Density adjusted to mean concentration D^{t}_{4}	Mean observed density D^{t}_{4}	Calculated D^{t}_{4}	Observed D^{t}_{4} minus calculated $D^{t}_{4} \times 10^6$
			t	D''^{t}_{4}						
1	10. 036	0. 798080	10	0. 798110	13	+ 8	0. 798118	0. 798116	0. 798118	0
14	10. 018	. 798108		. 798123		− 8	. 798115			−3
2	15. 005	. 793868	15	. 793872	21	+ 8	. 793880	. 793882	. 793879	+1
13	15. 022	. 793874		. 793893		− 8	. 793885			+6
3	19. 999	. 789610	20	. 789609	19	+ 8	. 789617	. 789618	. 789620	−3
12	20. 031	. 789602		. 789628		− 8	. 789620			0
4	25. 022	. 785307	25	. 785326	17	+ 8	. 785334	. 785334	. 785337	−3
11	25. 033	. 785315		. 785343		− 8	. 785335			−2
5	30. 008	. 781015	30	. 781022	10	+ 8	. 781030	. 781027	. 781026	+4
10	30. 010	. 781023		. 781032		− 8	. 781024			−2
6	34. 975	. 776698	35	. 776676	12	+ 8	. 776684	. 776682	. 776681	+3
9	34. 993	. 776694		. 776688		− 8	. 776680			−1
7	39. 947	. 772334	40	. 772287	20	+ 8	. 772295	. 772297	. 772298	−3
8	39. 966	. 772337		. 772307		− 8	. 772299			+1

Equation for adjustment of Δ: $\Delta = 15.4 + 0.214\ (7 - n)$.

Probable value of D^{t}_{4} from above determinations:. $D^{t}_{4} = 0.785337 - [859.3\ (t-25) + 0.57\ (t-25)^2 + 0.0062\ (t-25)^3]\ 10^{-6}$.

4. RÉSUMÉ OF RESULTS

By reduction and adjustment of experimental results there is derived for each mixture of alcohol and water investigated an equation for thermal expansion of the form:

$$D_4^t = D_4^{25} + \alpha(t-25) + \beta(t-25)^2 + \gamma(t-25)^3$$

D_4^{25} and the coefficients α, β, γ, having been determined from the experimental data.

The constant D_4^{25} for each mixture represents the mean density at 25° in terms of the density of water at 4° as the unit and is used for obtaining the mean concentration of the mixture used. A table showing the relation between density at 25° and concentration is given on page 424.

The assembled results of the experimental work on thermal expansion of alcohol-water mixtures are given in Table XXXVI. Included in this table are the corresponding coefficients for water calculated from the experimental work of Chappuis[1132] using the densities at 10, 15, 20, 25, 30, 35, 40° C, upon which the present work is based. The coefficients α, β, γ, are shown graphically as functions of the per cent of alcohol in Fig. 9.

Interpolated values of α, β, γ obtained by the graphical method are given for each integral per cent of alcohol in Table XXXVII*a*. The interpolation is carried to the number of figures shown for the purpose of avoiding arithmetic errors in the calculation of the final density Table XLIX in part 3. They should not be assumed correct to the last figure given. Furthermore, they can not be assumed as true except for the range of temperature used in their determination—viz, 10° C to 40° C.

In Table XXXVII*b* are given the coefficients A, B, C in the equation for thermal expansion of the form:

$$V_t = V_{25}[1 + A(t-25) + B(t-25)^2 + C(t-25)^3]$$

these coefficients having been calculated for each integral per cent of alcohol from the corresponding coefficients α, β, γ, given in Table XXXVII*a*.

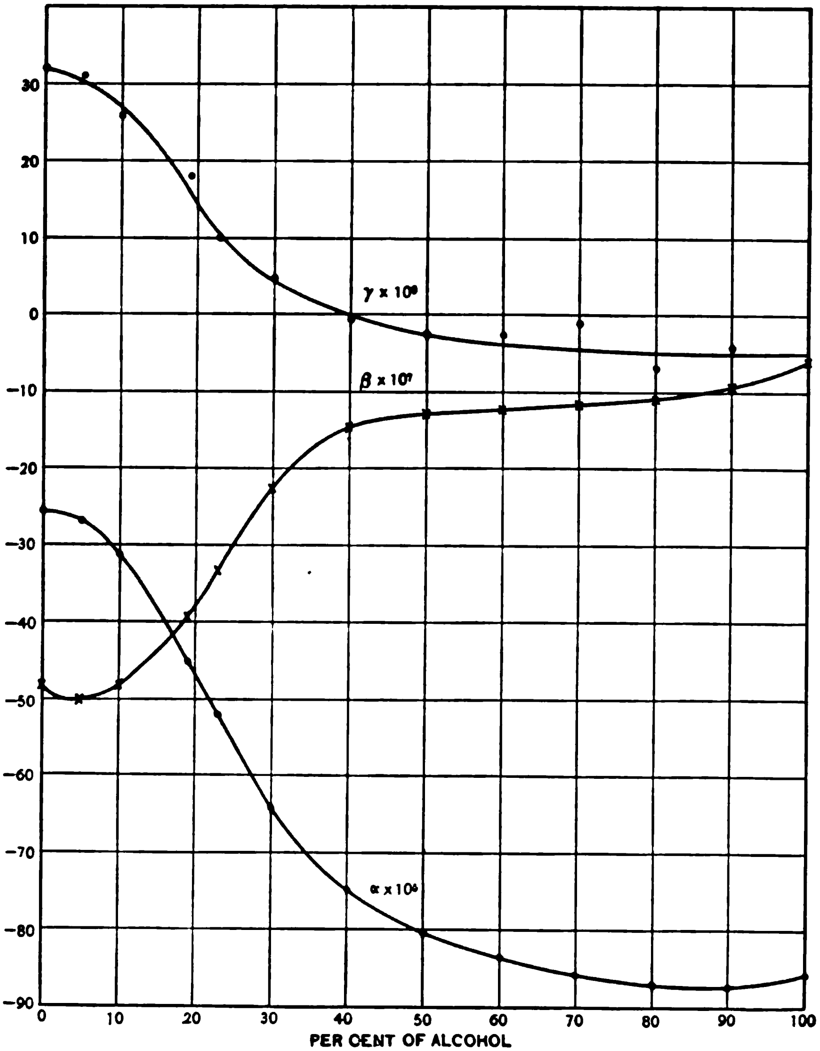


Fig. 9.—*Coefficients* α, β, γ

TABLE XXXVI

Thermal Expansion of Alcohol-Water Mixtures. Assembled Experimental Results

Equation: $D_4^t = D_4^{25} + \alpha(t-25) + \beta(t-25)^2 + \gamma(t-25)^3$. Temperature range: 10° C to 40° C

Per cent alcohol by weight	D_4^{25}	$\alpha \times 10^7$	$\beta \times 10^8$	$\gamma \times 10^{10}$
RESULTS FOR WATER ACCORDING TO CHAPPUIS'S DATA				
0	0.997077	−2565	−484	+319
RESULTS OF PRESENT INVESTIGATION				
4.907	0.988317	−2684	−502	+311
9.984	.980461	−3119	−484	+258
19.122	.967648	−4526	−393	+180
22.918	.962133	−5224	−331	+100
30.086	.950529	−6431	−226	+ 47
39.988	.931507	−7488	−145	− 4
49.961	.909937	−8033	−128	− 24
59.976	.887051	−8358	−121	− 24
70.012	.863380	−8581	−117	− 9
80.036	.839031	−8714	−108	− 69
90.037	.813516	−8746	− 93	− 51
99.913	.785337	−8593	− 57	− 62

TABLE XXXVIIa.—Interpolated values of α, β, γ, between 10°C to 40C°, in the equation:

$$D^t_4 = D^{25}_4 + \alpha(t-25) + \beta(t-25)^2 + \gamma(t-25)^3$$

Per cent alcohol by weight	$\alpha\times10^7$	$\beta\times10^8$	$\gamma\times10^9$	Per cent alcohol by weight	$\alpha\times10^7$	$\beta\times10^8$	$\gamma\times10^9$
0	−2565	−484	+31.9	50	*−8035*	*−128*	*−2*
1	−2574	−490	+32	51	−8074	−127	−3
2	−2591	−496	+32	52	−8111	−126	−3
3	−2613	−499	+31	53	−8147	−126	−3
4	−2646	−501	+31	54	−8181	−125	−3
5	*−2689*	*−502*	*+30*	55	−8212	−124	−3
6	−2745	−501	+30	56	−8244	−124	−3
7	−2816	−498	+29	57	−8274	−123	−4
8	−2901	−495	+29	58	−8302	−122	−4
9	−3003	−490	+28	59	−8330	−122	−4
10	*−3121*	*−484*	*+27*	60	*−8359*	*−121*	−4
11	−3244	−476	+26	61	−8384	−121	−4
12	−3374	−469	+25	62	−8410	−120	−4
13	−3513	−460	+24	63	−8435	−120	−4
14	−3662	−452	+23	64	−8459	−120	−4
15	−3817	−442	+22	65	−8482	−119	−4
16	−3978	−432	+20	66	−8503	−119	−4
17	−4146	−420	+19	67	−8524	−119	−4
18	−4322	−408	+18	68	−8544	−118	−4
19	*−4504*	*−395*	*+16*	69	−8564	−117	−4
20	−4686	−380	+14	70	*−8581*	*−117*	−5
21	−4870	−363	+13	71	−8599	−116	−5
22	−5055	−346	+11	72	−8614	−116	−5
23	*−5239*	*−329*	*+10*	73	−8629	−115	−5
24	−5419	−313	+ 9	74	−8643	−114	−5
25	−5601	−298	+ 8	75	−8657	−113	−5
26	−5778	−282	+ 7	76	−8669	−112	−5
27	−5951	−268	+ 6	77	−8681	−111	−5
28	−6114	−253	+ 6	78	−8692	−110	−5
29	−6271	−240	+ 5	79	−8703	−109	−5
30	*−6419*	*−227*	*+ 4*	80	*−8714*	*−108*	−5
31	−6554	−215	+ 4	81	−8723	−107	−5
32	−6685	−204	+ 3	82	−8731	−106	−5
33	−6810	−194	+ 3	83	−8739	−105	−5
34	−6929	−185	+ 2	84	−8745	−104	−5
35	−7040	−176	+ 2	85	−8751	−102	−5
36	−7144	−168	+ 1	86	−8753	−101	−5
37	−7239	−161	+ 1	87	−8754	− 99	−5
38	−7330	−155	+ 1	88	−8753	− 97	−5
39	−7413	−150	0	89	−8751	− 95	−5
40	*−7489*	*−145*	*0*	90	*−8746*	*− 93*	*−5*
41	−7561	−141	0	91	−8738	− 90	−5
42	−7627	−138	− 1	92	−8728	− 88	−5
43	−7689	−136	− 1	93	−8715	− 84	−5
44	−7748	−134	− 1	94	−8700	− 81	−5
45	−7802	−133	− 1	95	−8685	− 78	−5
46	−7855	−132	− 2	96	−8668	− 74	−5
47	−7903	−131	− 2	97	−8650	− 70	−5
48	−7950	−130	− 2	98	−8632	− 66	−5
49	−7993	−129	− 2	99	−8613	− 61	−5
50	*−8035*	*−128*	*− 2*	100	−8591	− 56	−5

TABLE XXXVIIb.—Values of A, B, C, between 10°C to 40°C, in the equation:

$$V_t = V_{25}[1 + A(t-25) + B(t-25)^2 + C(t-25)^3]$$

Per cent alcohol by weight	$A\times10^6$	$B\times10^7$	$C\times10^8$	Per cent alcohol by weight	$A\times10^6$	$B\times10^7$	$C\times10^8$
0	+257.2	+49.2	−2.9	50	+ 883.1	+21.9	+0.5
1	+259	+50	−3	51	+ 890	+22	+1
2	+261	+51	−3	52	+ 896	+22	+1
3	+264	+51	−3	53	+ 902	+22	+1
4	+267	+51	−3	54	+ 908	+22	+1
5	+272.1	+51.5	−2.7	55	+ 914	+22	+1
6	+278	+52	−3	56	+ 920	+22	+1
7	+286	+51	−3	57	+ 926	+22	+1
8	+295	+51	−3	58	+ 931	+22	+1
9	+306	+51	−2	59	+ 937	+22	+1
10	+318.3	+50.4	−2.4	60	+ 942.4	+22.5	+0.7
11	+331	+50	−2	61	+ 948	+23	+1
12	+345	+49	−2	62	+ 953	+23	+1
13	+360	+48	−2	63	+ 958	+23	+1
14	+376	+48	−2	64	+ 964	+23	+1
15	+392	+47	−2	65	+ 969	+23	+1
16	+409	+46	−2	66	+ 974	+23	+1
17	+427	+45	−2	67	+ 979	+23	+1
18	+446	+44	−1	68	+ 984	+23	+1
19	+465.4	+43.0	−1.2	69	+ 989	+23	+1
20	+485	+42	−1	70	+ 993.9	+23.4	+0.9
21	+505	+40	−1	71	+ 999	+24	+1
22	+525	+39	−1	72	+1003	+24	+1
23	+544.6	+37.2	−0.6	73	+1008	+24	+1
24	+564	+36	0	74	+1012	+24	+1
25	+584	+34	0	75	+1017	+24	+1
26	+604	+33	0	76	+1021	+24	+1
27	+623	+32	0	77	+1026	+24	+1
28	+641	+31	0	78	+1030	+24	+1
29	+658	+30	0	79	+1034	+24	+1
30	+675.2	+28.5	−0.1	80	+1038.5	+23.7	+0.9
31	+691	+27	0	81	+1043	+24	+1
32	+706	+26	0	82	+1047	+24	+1
33	+720	+26	0	83	+1051	+24	+1
34	+734	+25	0	84	+1055	+24	+1
35	+748	+24	0	85	+1059	+24	+1
36	+760	+24	0	86	+1062	+23	+1
37	+772	+23	0	87	+1066	+23	+1
38	+784	+23	0	88	+1069	+23	+1
39	+794	+22	0	89	+1072	+23	+1
40	+804.0	+22.0	+0.3	90	+1074.9	+23.0	+0.9
41	+814	+22	0	91	+1078	+23	+1
42	+822	+22	0	92	+1080	+23	+1
43	+831	+22	0	93	+1082	+22	+1
44	+839	+22	0	94	+1084	+22	+1
45	+847	+22	0	95	+1086	+22	+1
46	+855	+22	0	96	+1088	+21	+1
47	+862	+22	0	97	+1089	+21	+1
48	+870	+22	0	98	+1091	+20	+1
49	+876	+22	0	99	+1093	+20	+1
50	+883.1	+21.9	+0.5	100	+1094.3	+19.1	+0.8

PART 3

DENSITY OF ETHYL ALCOHOL AND OF ITS MIXTURES WITH WATER

By N. S. Osborne

Part 3 consists of the determination of the density at a single temperature, 25° C, of pure ethyl alcohol and of various mixtures of alcohol and water in accurately determined proportions and the derivation of alcoholometric tables.

VI. DESCRIPTION OF APPARATUS AND EXPERIMENTAL WORK

The fundamental determinations of the density of pure alcohol were made simultaneously with its preparation, as previously described. The compounding of the mixtures, using portions of the same purified material, and the determination of their densities followed these fundamental determinations.

The density determinations were made partly by the method of hydrostatic weighing, described in Part 2 of this paper (p. 371), and partly by the use of specially constructed picnometers. By the use of these picnometers the effect of dissolved air upon the density of alcohol and of its mixtures was investigated to ascertain its significance in alcoholometry.

1. THE PICNOMETERS

Three picnometers, specially designed for the purpose on the principle of the Ostwald-Sprengel type, were used. In the construction of these picnometers the elements desired were as follows:

(*a*) A form adapted to the rapid attainment of the constant temperature of a surrounding water bath.

(*b*) Means of filling with minimum contact of liquid with air.

(*c*) Protection after filling from change of weight by evaporation or absorption of moisture; and

(*d*) Precision of filling.

The form of the picnometers is illustrated in Figs. 10 and 11. They were all made of Jena 16^{III} glass and thoroughly annealed. They are adapted to immersion in the constant temperature bath already described. One of the picnometers (No. 274, Fig. 11) was of the Rudolphi[962] form, consisting of a hollow cylinder, which permits a rapid attainment of temperature but at expense of total volume. The others (Nos. 275 and 276, Fig. 11) were of the plain cylindrical form. The cap with stopcock attached, as shown in Fig. 11, is used to control the internal pressure when filling the picnometer. The bulb containing the liquid to be investigated is joined to the picnometer by the ground joint *b*. By proper manipulation, such as inclining the picnometer at a suitable angle and properly varying the air pressure, liquid is introduced into the picnometer. With the picnometer in position in the water bath, leaving only the upper portions of the capillaries emergent, the adjustment of the quantity of liquid is approximated as the temperature approaches constancy. Liquid may be introduced if necessary by means of a pipette placed with its tip to the aperture of the capillary with proper adjustment of pressure through the tube *c*. Small quantities may be removed by means of a strip of filter paper applied at the tip of the capillary. Enough liquid is removed to bring the meniscus just to the line *e* on the other capillary. The inside of the enlargement *d* of the tube is dried, either by means of filter paper or by a stream of dry air.

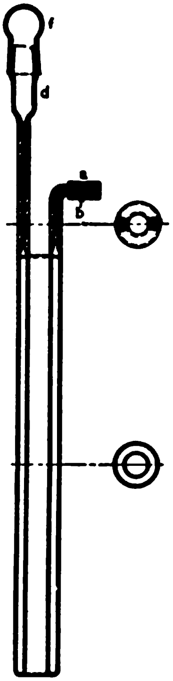


Fig. 10 (one-fourth size).

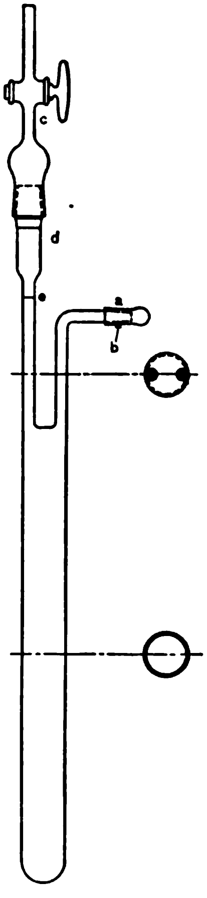


Fig. 11 (one-fourth size).

The picnometer itself serves as a sensitive thermo-indicator, and until the temperature becomes constant the final adjustment of the quantity of liquid can not be made. When the temperature appears steady, 5 or 10 minutes more are allowed as margin of safety, and the filling is then completed. The picnometer is closed to prevent evaporation or absorption of moisture by means of the cap *f*, shown in the illustration.

The constants of these picnometers are given in Table XXXVIII.

TABLE XXXVIII

Constants of Picnometers

Picnometer B. S. No.	External volume at 25° C	Mass	Internal volume at 25° C
	ml	g	ml
274	92.865	103.1393	46.1329
275	124.56	75.8659	87.4046
276	123.33	74.4672	86.0145

For the determinations of the volumes of these picnometers the density of water at $\frac{25^\circ}{4}$ C according to Chappuis[1132] (0.997077) was used.

2. EFFECT OF DISSOLVED AIR

The effect upon the density of absolute alcohol caused by dissolved air was first determined by the method of hydrostatic weighing. The density of the alcohol was observed after long contact with dry air. The sample in the tube was then evacuated until no more bubbles were evolved. The density was then redetermined. Dry air was then passed into the bottom of the tube and bubbled through the alcohol and the density again determined. This was repeated on a second sample of alcohol. The results are shown in Table XXXIX.

TABLE XXXIX

Effect of Dissolved Air on Density of Alcohol

SAMPLE OF FRACTION NO. 3 I

Original density at $\frac{25^\circ}{4}$ C	Density at $\frac{25^\circ}{4}$ C after evacuating	Density at $\frac{25^\circ}{4}$ C after passing in air
0.785094	0.785160	0.785134

FRACTION NO. 5 I

0.785041	0.785102	0.785061

Upon again saturating the alcohol with air the density did not return quite to its original value. This may be due to absorption of moisture. The above results indicate clearly that absorbed air decreases the density of absolute alcohol very appreciably. This is contrary to the experimental result obtained by Mendeléeff,[207, 241] who, by taking air-free alcohol and shaking it with supposedly dry air, observed an increase in the density.

The above preliminary experiments were repeated, using the picnometers for determining the densities. In the method of hydrostatic weighing the alcohol was in contact with the air while the determination was being made, thus leaving doubt as to the completeness of the observed effect. Hence it was anticipated that more consistent and uniform results would be possible with the picnometer. The results are shown in Table XL.

TABLE XL

Effect of Dissolved Air on Density of Alcohol

SAMPLE OF ABSOLUTE ALCOHOL IN PICNOMETER NO. 274

	$D^{25°}_{4}$	Change in density
After evacuating to remove air	0.785120	0.000065
After shaking with dry air	.785055	

SAMPLE NO. 5 I

	$D^{25°}_{4}$	Change in density
Original sample	0.785080	0.000091
After evacuating	.785171	
After shaking with dry air	.785097	
After shaking again with dry air	.785081	.000096
After reevacuating	.785177	
After shaking again with dry air	.785093	.000080
After reevacuating	.785173	
Mean change		.000083

The above results demonstrate the reproducibility of the effect, although not indicating to what extent it is dependent on the temperature. The mean observed effect of dissolved air at 25° is a decrease in density of 0.000083.

The quantity of air absorbed by absolute alcohol was approxamately determined by weighing, after evacuating to remove the air, a quantity of alcohol in a flask provided with a ground stopper, to which was attached a tube having two stopcocks with a bulb between. Dry air was admitted, shaken, and the flask again weighed. This was repeated until the weight became constant, indicating that no more air was absorbed. Ninety-three and fourteen hundredths (93.14) grams of alcohol absorbed .019 gram of air at about 20° C. This corresponds to about .13 cc of air for each cubic centimeter of alcohol.

The effect of dissolved air upon the density is so significant that the condition of alcohol as to whether air free or saturated with air must be specified if the density is used as a criterion of the completeness of dehydration.

Many experimenters neglect to state whether their alcohol is air free or air saturated. Mendeléeff[207] [241] states that the alcohol used by him was air free, and he used as a test for this condition the fact that when mixed with water no bubbles were given off. This does not seem to be a sufficiently definite test, since mixtures of alcohol and water may contain air, and from the low values obtained by Mendeléeff for the density of absolute alcohol and the method employed by him in obtaining it air free, it seems very doubtful if he removed more than a small part of the dissolved air.

The approximate effect of dissolved air upon the density of alcohol-water mixtures is derived later from the density determinations upon those mixtures.

3. DETERMINATION OF THE DENSITY OF ETHYL ALCOHOL

Having determined the magnitude of the effect of dissolved air upon the density, and having observed the greater uniformity in the density of the alcohol when saturated with air than when deprived of but left in contact with air, the density determinations to serve as criteria for comparison of different samples of supposedly pure alcohol were made in the air-saturated condition. The complete results of these determinations are given in Part 1.

In this place are given only the actual determinations upon the samples, which were regarded as being the purest prepared and on that account chosen to establish the value for the density of absolute alcohol.

These samples are designated by the number of the experiment in their preparation as described in detail in Part 1 of this paper. The complete record of observations and reductions to obtain the final mean value for the density of pure ethyl alcohol at $\frac{25}{4}$° C are given in Tables XLI to XLV.

TABLE XLI

Determinations of Density of Alcohol From Experiment IV Hydrostatic Weighing. Sinker No. 7

Date: Apr. 18, 1910. Record, vol. 646, p. 153

Corrected temperature		Mean corrected temperature	Apparent weight of sinker in liquid	True weight of sinker in liquid	Volume of sinker at observed temperature	Density of liquid at observed temperature	Density of liquid at 25° C	Fraction No.
Green 2499	Tonnelot 4653	t				D^t_4	D^{25}_4	
			g	g	ml			
25.008	25.010	25°010	62.5444	62.5358	47.71845	0.785088	0.785097	1
25.008	25.015		62.5443					
25.013	25.015	25°014	62.5459	62.5373	47.71845	.785057	.785069	2
25.008	25.020		62.5459					
25.013	25.015	25°014	62.5464	62.5378	47.71845	.785046	.785058	3
25.008	25.020		62.5464					
25.018	25.020	25°015	62.5466	62.5380	47.71846	.785042	.785055	4
25.008	25.015		62.5466					
25.013	25.020	25°014	62.5469	62.5382	47.71845	.785038	.785050	5
25.008	25.015		62.5468					
25.013	25 020	25°019	62.5468	62.5382	47.71846	.785038	.785054	6
25.018	25.025		62.5468					

Thermometer corrections: No. 2499, +0.008; No. 4653, +0.020. Observed air density: 0.00116 g/cm³. Buoyancy correction on weights: 0.0086 g. Mass of sinker: 99.9990 g.

TABLE XLII

Determinations of Density of Alcohol from Experiment VII. Hydrostatic Weighing: Sinker No. 7

Date: May 11, 1910. Record, vol. 646, p. 176

Corrected temperature		Mean corrected temperature t	Apparent weight of sinker in liquid	True weight of sinker in liquid	Volume of sinker at observed temperature	Density of liquid at observed temperature D_4^t	Density of liquid at 25° C D_4^{25}	Fraction No.
Green 2499	Tonnelot 4653							
			g	g	ml			
25.028	25.030	25.030	62.5469	62.5382	47.71847	0.785038	0.785064	1
25.028	25.035							
25.008	25.020	25.015	62.5465	62.5378	47.71846	.785046	.785059	2
25.013	25.020							
25.013	25.020	25.016	62.5465	62.5378	47.71846	.785046	.785060	3
25.013	25.020							

Thermometer corrections: No. 2499, +0.008; No. 4653, +0.020. Observed air density: 0.00116 g/cm³. Buoyancy correction on weights: 0.0087 g. Mass of sinker: 99.9990 g.

TABLE XLIII

Determinations of Density of Absolute Alcohol from Experiment XII

Hydrostatic Weighing: Sinker No. 7

Date: Apr. 7, 11, 12, 1910. Record, vol. 646, p. 147

Corrected temperature		Mean corrected temperature t	Apparent weight of sinker in liquid	True weight of sinker in liquid	Volume of sinker at observed temperature	Density of liquid at observed temperature D^t_4	Density of liquid at 25° C D^{25}_4	Fraction No.
Green 2499	Tonnelot 4653							
			g	g	ml			
25.008	25.010	25.012	62.5465	62.5378	47.71845	0.785046	0.785056	1
25.008	25.020		62.5466					
25.008	25.020	25.018	62.5464	62.5377	47.71846	.785048	.785063	[c] 1
25.023	25.020		62.5466					
25.013	25.015	25.016	62.5462	62.5375	47.71846	.785053	.785067	2
25.018	25.020		62.5463					
25.013	25.015	25.018	62.5469	62.5382	47.71846	.785038	.785053	3
25.018	25.025		62.5471					
24.998	25.005	25.005	62.5464	62.5377	47.71844	.785049	.785053	4
25.003	25.015		62.5465					
25.013	25.020	25.015	62.5463	62.5376	47.71846	.785050	.785063	5
25.008	25.020		62.5465					
24.993	25.000	24.996	62.5460	62.5372	47.7144	.785059	.785056	6
24.993	25.000		62.5459					

[c] After passing dry air through.

Thermometer corrections: No. 2499, +0.008; No. 4653, +0.020. Observed air density: 0.00118 g/cm³. Buoyancy correction on weights: 0.0088 g. Mass of sinker: 99.9990 g.

TABLE XLIV

Determinations of Density of Absolute Alcohol From Middle Fraction of Experiment VI

Record of Observations and Calculations. Record: Vol. 646, p. 166

Determined in picnometer B. S. No.	Date	Corrected temperature		Mean corrected temperature t	Apparent weight of picnometer in air	Air density Correction for air buoyancy	True weight of picnometer	Mass of contained liquid	Volume of contained liquid	Density of liquid at observed temperature D^{t}_{4}	Density of liquid at 25° D^{25}_{4}
		Green 2499	Tonnelot 4653								
					g		g	g	ml		
276	May 3, 1910	25.008	25.020	25.014	144.3581	0.001159	144.4826	68.6167	87.4046	0.785047	0.785059
		25.008	25.020			.1245					
274	May 4, 1910	24.998	25.005	25.002	139.2664	.001177	139.3562	36.2169	46.1329	.785056	.785058
		24.998	25.005			.0898					

Thermometer corrections: No. 2499, +0.008; No. 4653, +0.020.

TABLE XLV

The Density at $\frac{25^\circ}{4}$ of Pure Ethyl Alcohol Saturated with Air. Assembled Results of Most Satisfactory Experiments

Experiment number	Fraction number	Method of determination	Density at $\frac{25^\circ}{4}$ D_{4}^{25}	Observed density—mean density $\times 10^6$
IV	3	Hydrostatic weighing	0.785058	0
	4	.....do	.785055	−3
	5	.....do	.785050	−8
	6	.....do	.785054	−4
VI	2	Picnometer No. 276	.785059	+1
	2	Picnometer No. 274	.785058	0
VII	1	Hydrostatic weighing	.785064	+6
	2	.....do	.785059	+1
	3	.....do	.785060	+2
XII	1	.....do	.785063	+5
	2	.....do	.785067	+9
	3	.....do	.785053	−5
	4	.....do	.785053	−5
	5	.....do	.785063	+5
	6	.....do	.785056	−2
Mean			.785058	

Comparative examination of the results of the density determinations furnishes an index of the order of magnitude of the accidental errors. In Table XLV the average deviation from the mean of the 15 determinations is about 0.000004. The error of the mean due to accidental sources is within 0.000001.

The absolute accuracy of the densities is limited by the precision with which the thermometers have served to reproduce the International Hydrogen Scale. Two thermometers that were compared with the primary standards of the Bureau were always used. The corrected temperature indications of these thermometers rarely differed by as much as 0°.01. However, in consequence of the uncertainties inherent in the ice-point determinations, the effect of sticking of the meniscus, of small errors in reading, and the assumptions concerning the properties of verre dur glass that are necessarily made in the reproduction of the International Hydrogen Scale, the order of accuracy that has been attained in the reproduction of this temperature scale is, as nearly as can be estimated, about 0°.01 C, corresponding to about 0.000009 in density of pure alcohol at 25° C. Hence an accuracy of 1 unit of the fifth decimal place for this constant is all that can be expected.

As the result of these experiments 0.78506 is taken as the density at 25° C in grams per milliliter of pure ethyl alcohol saturated with air at ordinary atmospheric pressure.

4. PREPARATION OF THE MIXTURES—APPARATUS AND METHOD USED

In order to render the preparation of the mixtures as free as possible from causes of error in determining the proportions of alcohol and water, the apparatus shown in Fig. 12 was employed. It has been shown (p. 408) that pure alcohol at 25° C absorbs about 0.02 per cent of its own weight of air, which diminishes the density about 0.00008. Marek[614] has shown that the absorption of air does not appreciably change the density of water at 25° C.

When alcohol and water both saturated with air are mixed, air is given off. This constitutes a source of error in the composition which can not exceed 0.02 per cent and is doubtless considerably less. This error may, however, be avoided by using water and alcohol deprived of air. Another possible source of error when the alcohol and water used in mixtures are weighed at atmospheric pressure is the difficulty in ascertaining the density of the mixture of air and vapor in the vessel above the liquid. To avoid the two errors mentioned above and to enable also an approximate determination of the effect of dissolved air upon the mixtures of alcohol and water to be made, the mixing apparatus was constructed to permit the weighing of the liquids when evacuated to their vapor pressure. Referring to Fig. 12 it is seen that the apparatus consists of three parts—a bulb *B* with one opening, a three-way stopcock *D*, and a funnel-shaped vessel *A*, all provided with ground joints to permit their being joined together. In use the ground joints and the stopcock were lubricated sufficiently to render them air tight, using a rather soft mixture of rubber and vaseline. The procedure in making a mixture was as follows:

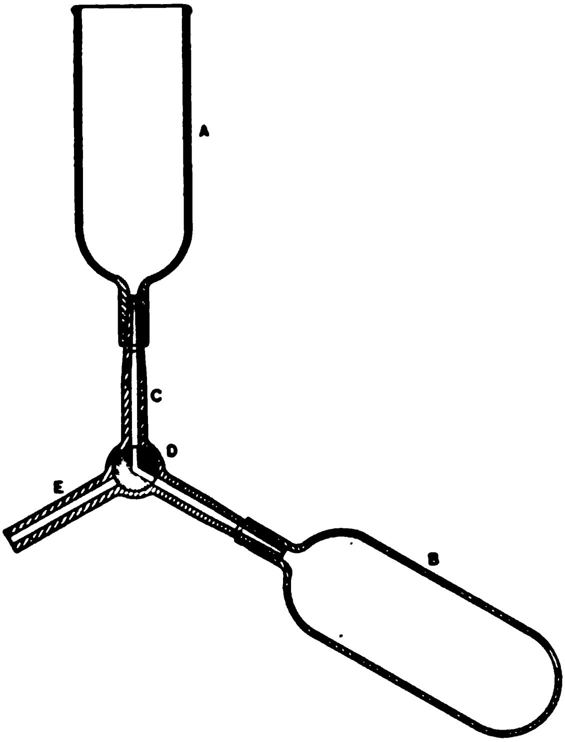


Fig. 12.—*Mixing apparatus (one-third size).*

The bulb with the three-way stopcock attached was first exhausted to remove the air and then closed and weighed. Next dry air was admitted and the stopcock removed. A suitable quantity of absolute alcohol was transferred to the bulb by means of a burette, only air which had been dried by P_2O_5 being allowed to come in contact with the alcohol. The stopcock was replaced and the bulb again evacuated to remove the dissolved air from the alcohol. By repeated exhaustion and thorough shaking of the bulb the alcohol was freed from air. The stopcock was turned so as to close the passage to the bulb and connect the two other passages *C* and *E* which were then thoroughly dried by forcing through a current of dry air. The closed bulb containing only air-free alcohol and alcohol vapor was then weighed.

The water used in making the mixtures was freed from air by subjecting it in a flask to repeated exhaustion to a low pressure and shaking until no more air could be removed. The amount of water required to make a mixture of the desired concentration was calculated from the known quantity of alcohol already in the bulb. The tubular opening in the stopcock was first filled with water just to the bottom of the funnel and then closed. The calculated amount of water was then measured into the funnel by means of a burette. On turning the stopcock to connect the funnel with the bulb the outside atmospheric pressure forced the water into the exhausted bulb containing the alcohol. When the water again reached just to the bottom of the funnel the cock was turned so as to close the bulb and open the other passages. The funnel was removed and the cock again dried as before, after which the bulb containing the air-free mixture was weighed. Thus the relative proportions of alcohol and water were determined. Notwithstanding these precautions for excluding air from the mixtures a slight amount could still be detected in the form of bubbles evolved when the water was mixed with the alcohol at the very low pressure present, but it was certainly much less in amount than would be present by any method of mixing at atmospheric pressure. The mixtures may be considered practically air free. The possibility of the grease being dissolved by the mixture was investigated by evaporating 75 cc of a 95 per cent mixture. Only 0.2 mg of residue was found ($\frac{1}{300000}$ part).

The dimensions of this mixing bulb are as follows:

External volume, with stopcock	cc	209.7
Internal volume	cc	152
Mass with stopcock	g	134.9

The balance used in making the mixtures was No. 5485, a Rueprecht analytical balance of 600-g load, similar in design to that used for the density determinations and described on page 377. This balance was sensitive to 0.5 mg. Corrections for displaced air were applied to all weighings. The weights used in making the mixtures were set No. 5157, the same as those used for the density determinations and described on page 377, except that those from 500 mg to 10 mg were the ones belonging to the balance. By previous test these were known to have no significant errors.

5. MATERIALS USED

The samples of absolute alcohol used in making the mixtures were portions of the distillates obtained in Experiments IV and XII, described in Part 1. The products of these experiments were regarded as of the greatest purity obtained.

The different samples of alcohol and the designations of the mixtures made from each, together with the determinations of density made at the time of use, are as follows:

SAMPLE 1

This sample was composed of fractions Nos. 2, 3, 4, and 5 from Experiment XII.

The density determinations were as follows:

Date	How made	$D\frac{25°}{4°}$
1910		
Apr. 7	Hydrostatic weighing	0.785058
Apr. 22	Picnometer No. 275	.785055
Apr. 29	Picnometer No. 276	.785043

From this sample were made mixtures designated as 95 D, 95 E, 95 F, 90 D, and 90 E.

SAMPLE 2

This sample was composed of fractions B, C, and D from Experiment IV.

The density determinations were as follows:

Date	How made	$D\frac{25°}{4°}$
1910		
Apr. 18	Hydrostatic weighing	0.785058
May 3	Picnometer No. 276	.785053
May 6	Picnometer No. 274	.785044
May 12	Picnometer No. 276	.785055
Do	do	.785047

From this sample were made mixtures designated 80 D, 70 D, 60 D, 50 D, 40 D. 65 D, 30 D, 20 D, 10 D, and 55 D.

SAMPLE 3

This sample was composed of fractions 2, 3, 4, 5, and 6 from Experiment IV. These portions are those upon which were made the original density determinations for Experiment IV. The density determinations were as follows:

Date	How made	$D\frac{25}{4}$
1910		
Apr. 18	Hydrostatic weighing	0.785057
May 25	Picnometer No. 276	.785069
May 26	do	.785052

From this sample were made mixtures designated 75 D, 85 D, 45 D, 35 D.

SAMPLE 4

This sample was fraction A from Experiment IV. The density determinations were as follows:

Date	How made	$D\frac{25}{4}$
1910		
Apr. 18	Hydrostatic weighing	0.785084
July 5	do	.785088

From this sample were made mixtures designated 25 D, 15 D, 5 D, 2 D, 6 D, 99 D, and 98 D.

With the exception of sample 4, the original density determinations indicated these samples to be as free from water as any produced. The determinations at different dates show that within limits of experimental error no change in density had occurred. This was to be expected, since the portions were kept in bottles with well-ground stoppers, the bottles themselves being kept in a desiccator containing lime. In transferring the alcohol from one vessel to another air was always used which had been dried by phosphorous pentoxide, thus avoiding contamination by atmospheric moisture.

Sample 4 shows a density higher than that determined for the purest alcohol, and in calculating the percentage of the mixtures the percentage of alcohol in this sample is taken as 99.992, this figure corresponding to the density 0.785086.

6. EXPERIMENTAL WORK AND REDUCTION OF RESULTS

The record of the preparation of the mixtures is given in journal form in Table XLVI.

Several of the mixtures found necessary for interpolation purposes, of such proportions that the exclusion of air in their preparation was not considered essential, were made in an ordinary weighing flask at atmospheric pressure and without evacuating, as shown in the second part of Table XLVI. The record of all the density determinations made upon the mixtures is given in journal form in Table XLVII.

TABLE XLVI

Record of Preparation of Mixtures

AIR-FREE MIXTURES MADE IN SPECIAL MIXING BULB

Designation of mixture	Made from sample No.	Date when made	True weight of alcohol	True weight of mixture	Per cent alcohol in mixture
		1910	g	g	
95 D	1	Apr. 23	66.202	69.820	94.818
95 E	1	Apr. 25	73.570	77.501	94.928
95 F	1	Apr. 26	101.054	106.414	94.963
90 D	1	...do	90.496	100.543	90.007
90 E	1	Apr. 30	93.542	103.931	90.004
80 D	2	May 4	79.350	99.254	79.946
70 D	2	...do	79.624	113.679	70.043
60 D	2	May 5	75.695	126.018	60.067
50 D	2	May 6	61.657	123.319	49.998
40 D	2	May 7	51.249	126.168	40.651
65 D	2	May 9	79.683	122.586	65.002
30 D	2	...do	39.894	132.968	30.003
20 D	2	May 10	27.077	135.321	20.009
10 D	2	May 11	13.434	134.231	10.008
55 D	2	May 13	66.701	121.336	54.972
75 D	3	May 25	66.413	88.592	74.965
85 D	3	May 26	92.576	108.868	85.035
45 D	3	May 27	58.140	129.345	44.950
35 D	3	May 28	47.300	134.876	35.069
25 D	4	June 1	34.798	138.692	[d] 25.088
15 D	4	June 3	20.243	134.845	[d] 15.010
5 D	4	...do	6.984	139.859	4.994

MIXTURES MADE IN ORDINARY FLASK WITHOUT EXCLUDING AIR

Designation of mixture	Made from sample No.	Date when made	True weight of alcohol	True weight of mixture	Per cent alcohol in mixture
		1910	g	g	
2 D	4	July 2	2.314	116.407	1.987
6 D	4	July 5	6.891	115.888	5.946
99 D	4	...do	91.774	92.732	[d] 98.957
98 D	4	...do	90.471	92.310	[d] 97.998

[d] Corrected for 0.01 per cent water in sample 4.

TABLE XLVII

Record of Determinations of Density of Mixtures

Assembled Results are Given in Table XLVIII

Designation of mixture	Date of density determination	Condition of mixture	Method of determination	Temperature of determination t	D^t_4	D^{25}_4
	1910					
95 D....	Apr. 23	Air free........	Picnometer 275...	24. 988	0. 800486	0. 800476
95 D....	...do.....	.....do.........	Picnometer 274...	25. 028	. 800440	. 800464
95 D....	...do.....	Air saturated...	.....do..........	25. 016	. 800427	. 800441
95 D....	Apr. 25	.....do.........	.....do..........	24. 997	. 800431	. 800428
95 E....	...do.....	Air free........	Picnometer 275...	24. 990	. 800160	. 800151
95 F....	Apr. 26	.....do.........	.....do..........	24. 970	. 800077	. 800051
95 F....	...do.....	.....do.........	.....do..........	24. 970	. 800087	. 800061
95 F....	...do.....	Air saturated...	.....do..........	24. 976	. 800023	. 800004
95 F....	...do.....	.....do.........	Hydrostatic......	24. 979	. 800031	. 800013
95 F....	...do.....	.....do.........	.....do..........	24. 978	. 800024	. 800005
95 F....	...do.....	.....do.........	.....do..........	24. 976	. 800033	. 800012
95 F....	Apr. 27	.....do.........	.....do..........	24. 999	. 800018	. 800017
90 D....	...do.....	Air free........	Picnometer 275...	25. 003	. 813620	. 813623
90 D....	...do.....	Air saturated...	.....do..........	24. 989	. 813608	. 813598
90 D....	Apr. 29	.....do.........	Hydrostatic......	25. 008	. 813591	. 813598
90 E....	Apr. 30	Air free........	Picnometer 276...	25. 008	. 813634	. 813641
90 E....	...do.....	Air saturated...	.....do..........	25. 003	. 813614	. 813617
80 D....	May 4	Air free........	.....do..........	24. 993	. 839297	. 839291
80 D....	...do.....	Air saturated...	.....do..........	24. 993	. 839245	. 839239
80 D....	...do.....	.....do.........	Hydrostatic......	25. 008	. 839248	. 839255
70 D....	...do.....	Air free........	Picnometer 276...	24. 992	. 863344	. 863337
70 D....	May 5	Air saturated...	Hydrostatic......	25. 008	. 863289	. 863296
60 D....	...do.....	Air free........	Picnometer 276...	25. 008	. 886856	. 886863
60 D....	...do.....	Air saturated...	.....do..........	25. 000	. 886840	. 886840
60 D....	...do.....	.....do.........	Picnometer 274...	25. 008	. 886820	. 886827
60 D....	May 6	.....do.........	Hydrostatic......	25. 008	. 886831	. 886838
50 D....	...do.....	Air free........	Picnometer 276...	25. 003	. 909861	. 909863
50 D....	...do.....	Air saturated...	.....do..........	25. 003	. 909859	. 909861
50 D....	May 7	.....do.........	Picnometer 274...	25. 006	. 909847	. 909852
40 D....	...do.....	Air free........	Picnometer 276...	24. 996	. 930140	. 930139
40 D....	...do.....	Air saturated...	.....do..........	24. 994	. 930140	. 930135
65 D....	May 9	Air free........	.....do..........	25. 016	. 875262	. 875276
65 D....	...do.....	Air saturated...	.....do..........	25. 013	. 875253	. 875264
30 D....	May 10	Air free........	.....do..........	25. 004	. 950682	. 950685
30 D....	...do.....	Air saturated...	.....do..........	24. 994	. 950671	. 950667
20 D....	...do.....	Air free........	.....do..........	24. 983	. 966394	. 966393
20 D....	...do.....	Air saturated...	.....do..........	24. 988	. 966380	. 966379
10 D....	May 12	Air free........	.....do..........	25. 000	. 980431	. 980431
10 D....	...do.....	Air saturated...	.....do..........	25. 000	. 980422	. 980422
55 D....	May 13	Air free........	.....do..........	24. 990	. 898584	. 898576
55 D....	...do.....	Air saturated...	.....do..........	24. 989	. 898575	. 898566
75 D....	May 25	Air free........	.....do..........	24. 986	. 851456	. 851444
75 D....	...do.....	Air saturated...	.....do..........	24. 970	. 851447	. 851421
85 D....	May 26	Air free........	.....do..........	24. 994	. 826547	. 826542
85 D....	...do.....	Air saturated...	.....do..........	24. 996	. 826511	. 826507

TABLE XLVII—Continued

Record of Determinations of Density of Mixtures—Continued

Designation of mixture	Date of density determination	Condition of mixture	Method of determination	Temperature of determination t	D^t_4	D^{25}_4
	1910					
45 D....	May 27	Air free........	Picnometer 276 ..	24.983	0.920993	0.920980
45 D....	...do.....	Air saturated...	.....do...........	24.973	.920980	.920959
35 D....	May 28	Air free........	.....do...........	24.980	.941343	.941329
35 D....	...do.....	Air saturated...	.....do...........	24.986	.941336	.941326
25 D....	June 2	Air free........	.....do...........	24.983	.958810	.958800
25 D....	...do.....	Air saturated...	.....do...........	24.983	.958820	.958810
15 D....	June 3	Air free........	.....do...........	24.986	.973333	.973328
15 D....	...do.....	Air saturated...	.....do...........	24.980	.973339	.973331
5 D....	June 6	Air free........	.....do...........	24.992	.988171	.988169
5 D....	...do.....	Air saturated...	.....do...........	24.996	.988177	.988176
2 D....	July 2	.....do.........	Hydrostatic......	25.070	.993365	.993383
6 D....	July 5	.....do.........	.....do...........	25.045	.986636	.986648
99 D....	...do.....	.....do.........	.....do...........	25.046	.788227	.788267
98 D....	...do.....	.....do.........	.....do...........	25.042	.791140	.791176

The assembled results and their reduction to integral percentages are given in Table XLVIII. In this table also, columns 5 and 6, are given the observed and calculated values for the effect of dissolved air on the density.

The linear equation,

$$Y = 0.3326\,X$$

in which Y represents the difference in density between air-free and air-saturated mixture, X the percentage of alcohol, and in which the coefficient is determined by a least square adjustment of the observed values of Y is used in calculating column 6.

It is seen that for mixtures of 95 per cent and under this equation represents the results within the limits of error of the determinations. If, however, the result for pure alcohol is considered, i. e., 0.000083, the equation is not satisfied within 0.00005. The results for this effect of air on the density of mixtures are given here not within any claim to their precision, but merely as a rough index of the possible effect. Further investigation by more exact methods would be of interest.

TABLE XLVIII

Determination of Density of Alcohol-Water Mixtures, Assembled Results and Reductions

Designation of mixture	Per cent alcohol by weight	Mean observed density at $\frac{25°}{4}$		Air free $D\frac{25}{4}$ minus air saturated $D\frac{25}{4}$		Reduction of air saturated D_{25} to integral per cent	
		Air free	Air saturated	Obs ×10⁶	Cal ×10⁶	Per cent alcohol by weight	Density at $\frac{25°}{4}$ C
2 D	1.987	....	0.993383	....	......	2	0.993359
5 D	4.994	0.988169	.988176	− 7	2	5	.988166
6 D	5.946	....	.986648	....	......	6	.986563
10 D	10.008	.980431	.980422	9	3	10	.980434
15 D	15.010	.973328	.973331	− 3	5	15	.973345
20 D	20.009	.966393	.966379	14	7	20	.966392
25 D	25.088	.958800	.958810	−10	8	25	.958946
30 D	30.003	.950685	.950667	18	10	30	.950672
35 D	35.069	.941329	.941326	3	12	35	.941459
40 D	40.651	.930139	.930135	4	13	40	.931483
45 D	44.950	.920980	.920959	21	15	45	.920850
50 D	49.998	.909863	.909856	7	17	50	.909852
55 D	54.972	.898576	.898566	10	18	55	.898502
60 D	60.067	.886863	.886835	28	20	60	.886990
65 D	65.002	.875276	.875264	12	22	65	.875269
70 D	70.043	.863337	.863296	41	23	70	.863399
75 D	74.965	.851444	.851421	23	25	75	.851336
80 D	79.946	.839291	.839247	44	27	80	.839114
85 D	85.035	.826542	.826507	35	28	85	.826596
90 D	90.007	.813623	.813598	25	30	90	.813622
90 E	90.004	.813641	.813617	24	30		
95 D	94.818	.800470	.800434	36	32	95	.799912
95 F	94.963	.800056	.800010	46	32		
98 D	97.998	....	.791176	....	......	98	.791170
99 D	98.957	....	.788267	....	......	99	.788135
100 (mean value)	100.000	.785141	.785058	83	33	100	.785058

Table XLIX gives for every integral per cent the density at 10°, 15°, 20°, 25°, 30°, 35°, and 40° C in terms of the density of water at 4° C of mixtures of ethyl alcohol and water when saturated with air. The densities at 25° of integral per cents given in this table are derived from the experimental results of Table XLVIII by a method of interpolation partly graphical and partly analytical, the details of which are not of sufficient interest to be given here. The densities at 10°, 15°, 20°, 30°, 35°, and 40° are calculated from the densities at 25° by use of the equation

$$D'^{t}_{4} = D^{25}_{4} + \alpha(t-25) + \beta(t-25)^2 + \gamma(t-25)^3$$

The values of α, β, and γ are given in Table XXXVIIa. Page 402.

7. ALCOHOLOMETRIC DENSITY TABLE

TABLE XLIX

Density of Mixtures of Ethyl Alcohol and Water D_4^t

Per cent alcohol by weight	Temperature t						
	10° C	15° C	20° C	25° C	30° C	35° C	40° C
0	0. 99973	0. 99913	0. 99823	0. 99708	0. 99568	0. 99406	0. 99225
1	. 99785	. 99725	. 99636	. 99520	. 99379	. 99217	. 99034
2	. 99602	. 99542	. 99453	. 99336	. 99194	. 99031	. 98846
3	. 99426	. 99365	. 99275	. 99157	. 99014	. 98849	. 98663
4	. 99258	. 99195	. 99103	. 98984	. 98839	. 98672	. 98485
5	. 99098	. 99032	. 98938	. 98817	. 98670	. 98501	. 98311
6	. 98946	. 98877	. 98780	. 98656	. 98507	. 98335	. 98142
7	. 98801	. 98729	. 98627	. 98500	. 98347	. 98172	. 97975
8	. 98660	. 98584	. 98478	. 98346	. 98189	. 98009	. 97808
9	. 98524	. 98442	. 98331	. 98193	. 98031	. 97846	. 97641
10	. 98393	. 98304	. 98187	. 98043	. 97875	. 97685	. 97475
11	. 98267	. 98171	. 98047	. 97897	. 97723	. 97527	. 97312
12	. 98145	. 98041	. 97910	. 97753	. 97573	. 97371	. 97150
13	. 98026	. 97914	. 97775	. 97611	. 97424	. 97216	. 96989
14	. 97911	. 97790	. 97643	. 97472	. 97278	. 97063	. 96829
15	. 97800	. 97669	. 97514	. 97334	. 97133	. 96911	. 96670
16	. 97692	. 97552	. 97387	. 97199	. 96990	. 96760	. 96512
17	. 97583	. 97433	. 97259	. 97062	. 96844	. 96607	. 96352
18	. 97473	. 97313	. 97129	. 96923	. 96697	. 96452	. 96189
19	. 97363	. 97191	. 96997	. 96782	. 96547	. 96294	. 96023
20	. 97252	. 97068	. 96864	. 96639	. 96395	. 96134	. 95856
21	. 97139	. 96944	. 96729	. 96495	. 96242	. 95973	. 95687
22	. 97024	. 96818	. 96592	. 96348	. 96087	. 95809	. 95516
23	. 96907	. 96689	. 96453	. 96199	. 95929	. 95643	. 95343
24	. 96787	. 96558	. 96312	. 96048	. 95769	. 95476	. 95168
25	. 96665	. 96424	. 96168	. 95895	. 95607	. 95306	. 94991
26	. 96539	. 96287	. 96020	. 95738	. 95442	. 95133	. 94810
27	. 96406	. 96144	. 95867	. 95576	. 95272	. 94955	. 94625
28	. 96268	. 95996	. 95710	. 95410	. 95098	. 94774	. 94438
29	. 96125	. 95844	. 95548	. 95241	. 94922	. 94590	. 94248
30	. 95977	. 95686	. 95382	. 95067	. 94741	. 94403	. 94055
31	. 95823	. 95524	. 95212	. 94890	. 94557	. 94214	. 93860
32	. 95665	. 95357	. 95038	. 94709	. 94370	. 94021	. 93662
33	. 95502	. 95186	. 94860	. 94525	. 94180	. 93825	. 93461
34	. 95334	. 95011	. 94679	. 94337	. 93986	. 93626	. 93257
35	. 95162	. 94832	. 94494	. 94146	. 93790	. 93425	. 93051
36	. 94986	. 94650	. 94306	. 93952	. 93591	. 93221	. 92843
37	. 94805	. 94464	. 94114	. 93756	. 93390	. 93016	. 92634
38	. 94620	. 94273	. 93919	. 93556	. 93186	. 92808	. 92422
39	. 94431	. 94079	. 93720	. 93353	. 92979	. 92597	. 92208
40	. 94238	. 93882	. 93518	. 93148	. 92770	. 92385	. 91992
41	. 94042	. 93682	. 93314	. 92940	. 92558	. 92170	. 91774
42	. 93842	. 93478	. 93107	. 92729	. 92344	. 91952	. 91554
43	. 93639	. 93271	. 92897	. 92516	. 92128	. 91733	. 91332
44	. 93433	. 93062	. 92685	. 92301	. 91910	. 91513	. 91108
45	. 93226	. 92852	. 92472	. 92085	. 91692	. 91291	. 90884
46	. 93017	. 92640	. 92257	. 91868	. 91472	. 91069	. 90660
47	. 92806	. 92426	. 92041	. 91649	. 91250	. 90845	. 90434
48	. 92593	. 92211	. 91823	. 91429	. 91028	. 90621	. 90207
49	. 92379	. 91995	. 91604	. 91208	. 90805	. 90396	. 89979
50	. 92162	. 91776	. 91384	. 90985	. 90580	. 90168	. 89750

TABLE XLIX—Continued

Per cent alcohol by weight	Temperature t						
	10° C	15° C	20° C	25° C	30° C	35° C	40° C
50	0. 92162	0. 91776	0. 91384	0. 90985	0. 90580	0. 90168	0. 89750
51	. 91943	. 91555	. 91160	. 90760	. 90353	. 89940	. 89519
52	. 91723	. 91333	. 90936	. 90534	. 90125	. 89710	. 89288
53	. 91502	. 91110	. 90711	. 90307	. 89896	. 89479	. 89056
54	. 91279	. 90885	. 90485	. 90079	. 89667	. 89248	. 88823
55	. 91055	. 90659	. 90258	. 89850	. 89437	. 89016	. 88589
56	. 90831	. 90433	. 90031	. 89621	. 89206	. 88784	. 88356
57	. 90607	. 90207	. 89803	. 89392	. 88975	. 88552	. 88122
58	. 90381	. 89980	. 89574	. 89162	. 88744	. 88319	. 87888
59	. 90154	. 89752	. 89344	. 88931	. 88512	. 88085	. 87650
60	. 89927	. 89523	. 89113	. 88699	. 88278	. 87851	. 87417
61	. 89698	. 89293	. 88882	. 88466	. 88044	. 87615	. 87180
62	. 89468	. 89062	. 88650	. 88233	. 87809	. 87379	. 86943
63	. 89237	. 88830	. 88417	. 87998	. 87574	. 87142	. 86705
64	. 89006	. 88597	. 88183	. 87763	. 87337	. 86905	. 86466
65	. 88774	. 88364	. 87948	. 87527	. 87100	. 86667	. 86227
66	. 88541	. 88130	. 87713	. 87291	. 86863	. 86429	. 85987
67	. 88308	. 87895	. 87477	. 87054	. 86625	. 86190	. 85747
68	. 88074	. 87660	. 87241	. 86817	. 86387	. 85950	. 85507
69	. 87839	. 87424	. 87004	. 86579	. 86148	. 85710	. 85266
70	. 87602	. 87187	. 86766	. 86340	. 85908	. 85470	. 85025
71	. 87365	. 86949	. 86527	. 86100	. 85667	. 85228	. 84783
72	. 87127	. 86710	. 86287	. 85859	. 85426	. 84986	. 84540
73	. 86888	. 86470	. 86047	. 85618	. 85184	. 84743	. 84297
74	. 86648	. 86229	. 85806	. 85376	. 84941	. 84500	. 84053
75	. 86408	. 85988	. 85564	. 85134	. 84698	. 84257	. 83809
76	. 86168	. 85747	. 85322	. 84891	. 84455	. 84013	. 83564
77	. 85927	. 85505	. 85079	. 84647	. 84211	. 83768	. 83319
78	. 85685	. 85262	. 84835	. 84403	. 83966	. 83523	. 83074
79	. 85442	. 85018	. 84590	. 84158	. 83720	. 83277	. 82827
80	. 85197	. 84772	. 84344	. 83911	. 83473	. 83029	. 82578
81	. 84950	. 84525	. 84096	. 83664	. 83224	. 82780	. 82329
82	. 84702	. 84277	. 83848	. 83415	. 82974	. 82530	. 82079
83	. 84453	. 84028	. 83599	. 83164	. 82724	. 82279	. 81828
84	. 84203	. 83777	. 83348	. 82913	. 82473	. 82027	. 81576
85	. 83951	. 83525	. 83095	. 82660	. 82220	. 81774	. 81322
86	. 83697	. 83271	. 82840	. 82405	. 81965	. 81519	. 81067
87	. 83441	. 83014	. 82583	. 82148	. 81708	. 81262	. 80811
88	. 83181	. 82754	. 82323	. 81888	. 81448	. 81003	. 80552
89	. 82919	. 82492	. 82062	. 81626	. 81186	. 80742	. 80291
90	. 82654	. 82227	. 81797	. 81362	. 80922	. 80478	. 80028
91	. 82386	. 81959	. 81529	. 81094	. 80655	. 80211	. 79761
92	. 82114	. 81688	. 81257	. 80823	. 80384	. 79941	. 79491
93	. 81839	. 81413	. 80983	. 80549	. 80111	. 79669	. 79220
94	. 81561	. 81134	. 80705	. 80272	. 79835	. 79393	. 78947
95	. 81278	. 80852	. 80424	. 79991	. 79555	. 79114	. 78670
96	. 80991	. 80566	. 80138	. 79706	. 79271	. 78831	. 78388
97	. 80698	. 80274	. 79846	. 79415	. 78981	. 78542	. 78100
98	. 80399	. 79975	. 79547	. 79117	. 78684	. 78247	. 77806
99	. 80094	. 79670	. 79243	. 78814	. 78382	. 77946	. 77507
100	. 79784	. 79360	. 78934	. 78506	. 78075	. 77641	. 77203

TABLE L

Comparison of Densities of Various Per Cents Alcohol by Weight

Per cent alcohol by weight	Bureau of Standards[1376] 1910	Mendeléeff's values recalculated by—						Mendeléeff[237,241] 1865[f]	B. S. 1910—Mend.	Kreitling[646] 1892[g]	B. S. 1910—Kreit.
		Bureau of Standards[1216] 1909	B. S. 1910—B. S. 1909	E. W. Merley[1466] 1904	B. S. 1910—Merley	K. Normal-Eichungs-Komm.[64] 1893[e]	B. S. 1910—K. N. E. K.				
	$D\frac{20^\circ}{4^\circ}C$	$D\frac{20^\circ}{4^\circ}C$	Units of fifth place	$D\frac{20^\circ}{4^\circ}C$	Units of fifth place	$D\frac{20^\circ}{4^\circ}C$	Units of fifth place	$D\frac{20^\circ}{4^\circ}C$	Units of fifth place	$D\frac{20^\circ}{4^\circ}C$	Units of fifth place
0	99823	99824	−1	99824	− 1	99824	− 1	99831	− 8	99823	0
5	98939	98936	+3	98927	+12	98948	− 9	98945	− 6	98941	− 2
10	98187	98185	+2	98189	− 2	98197	−10	98195	− 8	98194	− 7
15	97514	97522	−8	97519	− 5	97533	−19	97527	−13	97531	−17
20	96864	96870	−6	96872	− 8	96877	−13	96877	−13	96877	−13
25	96168	96171	−3	96175	− 7	96171	− 3	96185	−17	96175	− 7
30	95382	95385	−3	95387	− 5	95381	+ 1	95403	−21	95380	+ 2
35	94494	94499	−5	94506	−12	94496	− 2	94514	−20	94503	− 9
40	93519	93524	−5	93525	− 6	93523	− 4	93511	+ 8	93527	− 8
45	92472	92480	−8	92483	−11	92484	−12	92493	−21	92485	−13
50	91384	91386	−2	91386	− 2	91393	− 9	91400	−16	91392	− 8
55	90258	90262	−4	90263	− 5	90265	− 7	90275	−17	90263	− 5
60	89114	89115	−1	89115	− 1	89115	− 1	89129	−15	89114	0
65	87948	87950	−2	87950	− 2	87946	+ 2	87961	−13	87948	0
70	86766	86770	−4	86769	− 3	86762	+ 4	86781	−15	86767	− 1
75	85564	85570	−6	85569	− 5	85562	+ 2	85580	−16	85567	− 3
80	84344	84349	−5	84348	− 4	84339	+ 5	84366	−22	84347	− 3
85	83095	83097	−2	83097	− 2	83091	+ 4	83115	−20	83099	− 4
90	81797	81795	+2	81794	+ 3	81795	+ 2	81801	− 4	81801	− 4
95	80423	80417	+6	80421	+ 2	80424	− 1	80433	−10	80424	− 1
100	78934	78933	+1	78932	+ 2	78939	− 5	78945	−11	78930	+ 4

[e] Recalculated from Mendeléeff's values of $D\frac{20^\circ}{15^\circ}C$, given in Landolt and Börnstein (1905).

[f] Mendeléeff's[237,241] uncorrected values.

[g] Recalculated from Kreitling's[646] values of $D\frac{20^\circ}{15^\circ}C$.

TABLE LI

Comparison of Densities of Various Per Cents Alcohol by Volume at 60° F (15°56 C)

Per cent alcohol by volume at 60° F	Bureau of Standards[1376] 1910	Mendeléeff's values recalculated by—				McCulloch[119h]	B. S. 1910—McC.	Squibb[488 i]	B. S. 1910—Squibb	Gilpin,[8] Drinkwater,[102] and Squibb[488 i]	B. S. 1910—G., D., and S
		Bureau of Standards[1216] 1909	B. S. 1910—B. S. 1909	K. Normal-Eichungs Komm.[646]	B. S. 1910—K. N. E. K.						
	$D\frac{60^\circ}{60^\circ}F$	$D\frac{60^\circ}{60^\circ}F$	Units of fifth place	$D\frac{60^\circ}{60^\circ}F$	Units of fifth place	$D\frac{60^\circ}{60^\circ}F$	Units of fifth place	$D\frac{60^\circ}{60^\circ}F$	Units of fifth place	$D\frac{60^\circ}{60^\circ}F$	Units of fifth place
0	1.00000	1.00000	0	1.00000	0	1.00000	0	1.0000	0	1.00000	0
5	.99282	.99283	− 1	.99279	+ 3	.99289	− 7	.9930	−18	.99281	+ 1
10	.98659	.98658	+ 1	.98657	+ 2	.98663	− 4	.9869	−31	.98660	− 1
15	.98104	.98112	− 8	.98114	−10	.98114	−10	.9815	−46	.98114	−10
20	.97595	.97607	−12	.97608	−13	.97600	− 5	.9760	− 5	.97608	−13
25	.97086	.97096	−10	.97097	−11	.97087	− 1	.9709	− 4	.97097	−11
30	.96535	.96540	− 5	.96541	− 6	.96541	− 6	.9652	+15	.96541	− 6
35	.95910	.95909	+ 1	.95910	0	.95915	− 5	.9593	−20	.95910	0
40	.95179	.95184	− 5	.95185	− 6	.95192	−13	.9519	−11	.95185	− 6
45	.94350	.94360	−10	.94364	−14	.94359	− 9	.9434	+10	.94364	−14
50	.93428	.93440	−12	.93445	−17	.93437	− 9	.9343	− 2	.93443	−15
55	.92419	.92435	−16	.92439	−20	.92427	− 8	.9242	− 1		
60	.91343	.91356	−13	.91358	−15	.91346	− 3	.9135	− 7		
65	.90202	.90210	− 8	.90214	−12	.90211	− 9	.9025	−48		
70	.88999	.89004	− 5	.89010	−11	.89003	− 4	.8900	− 1		
75	.87729	.87734	− 5	.87740	−11	.87730	− 1	.8769	+39		
80	.86381	.86389	− 8	.86395	−14	.86384	− 3	.8639	− 9		
85	.84942	.84955	−13	.84961	−19	.84950	− 8	.8496	−18		
90	.83381	.83394	−13	.83400	−19	.83385.	− 4	.8340	−19		
95	.81604	.81611	− 7	.81616	−12	.81598	+ 6	.8164	−36		
100	.79388	.79387	+ 1	.79391	− 3	.79461	−73	.7946	−72		

[h] From the table given in Gauger's Manual.[216,1211]

[i] Bulletin No. 107 (Revised) Bureau of Chemistry.[1265]

8. REVIEW OF RESULTS

A comparison between the results of this investigation and those of other experimenters is shown in Tables L and LI. The results compared are the basis of several of the most important alcoholometric tables in general use at the present time. In order to render the different tables directly comparable, they have, as far as possible, been reduced to the same temperature basis.

In regard to the accuracy of Mendeléeff's results, reference to his publication [241] of 1869 and examination of the tables of densities which he calculated by least square adjustment of the experimental data, shows differences between the observed and calculated results of several units of the fourth decimal place. Whether these discrepancies are attributed to experimental error or arise from defective adjustment, they furnish an indication of the magnitude of unexplained discordance. The adjusted values agree slightly better than the observed with the results presented here and have been used for comparison.

Explanation of the outstanding differences shown in the preceding comparison tables will not here be undertaken further than to suggest the possibility that a greater degree of refinement in apparatus and experimental conditions with regard to temperature control and measurement in particular have in the present work enabled the attainment of higher precision.

Taking into account all sources of error it would be difficult to account for any error in Table XLIX greater than .00004; however, the desirability of further experimental work to ascertain the accuracy with which the fundamental determinations can be repeated by another observer is suggested.

In conclusion, the author acknowledges indebtedness to Mr. H. W. Bearce for valuable assistance in the observations and calculations involved in the determinations.

WASHINGTON, August 1, 1910

PART 4

DENSITY OF ETHYL ALCOHOL AND OF ITS MIXTURES WITH WATER. (A CONFIRMATORY SERIES)

By H. W. Bearce

During December, 1910, and January, 1911, the work on ethyl alcohol and its mixtures with water was continued. A second and independent series of mixtures were prepared and their densities measured at 15° and 25° for the purpose of determining the reproducibility of the results already obtained. By making the determinations at both 15° and 25° it was possible to verify, at the same time, the densities at 25° and the rate of change of density between 15° and 25°.

VII. DESCRIPTION OF EXPERIMENTAL WORK

1. MATERIAL, APPARATUS, AND METHODS

The alcohol used for making the mixtures was from two new distillations of the same original material as that used in the first series.

A mixture of fractions 4, 6, and 8 of Experiment XIV (see p. 366, pt. 1) was used for making the mixtures designated in Table LIV as 10 E, 20 E, 30 G, 40 E, 60 E, 70 E, 80 E, and 90 E, while for making those mixtures designated as 20 G, 30 H, 50 E, and 70 F the mixed fractions for Experiment XV were used. The alcohol used for making the mixtures was in each case, immediately after distillation, placed in a glass receptacle closed by closely fitting ground joints. This receptacle was provided with a burette attachment through which the alcohol was drawn off as required for making the mixtures. Only air that had been passed through drying tubes containing calcium chloride and phosphorous pentoxide was allowed to come in contact with the alcohol.

The balances, weights, thermometers, sinker, and apparatus for controlling the temperature were those already described

All density determinations were made by the method of hydrostatic weighing. The methods of procedure that have been described in detail in parts 2 and 3 of this paper were, as far as possible, followed in part 4.

During this series of measurements ice-point readings of the thermometers were not taken after each temperature, but were taken at intervals sufficiently short to have shown any considerable change had it occurred. It is believed that the mean of the extended series of ice-point readings available from earlier work with the same thermometers, at the same temperatures, gives as consistent and as reliable results as could be obtained by individual readings.

For making the mixtures an ordinary graduated, stoppered flask was used instead of the special mixing bulb described in part 3. All mixtures were made with twice-distilled, air-free water, and to prevent expulsion of air bubbles at the higher temperature the mixtures were freed from excess of dissolved air by evacuating to about 1 cm of mercury and thoroughly shaking. At the time of determination they were probably in an approximately air-saturated condition.

In the following tabulated results no determinations have been omitted except those of two mixtures which were spoiled in the process of making and one other in which the temperature conditions were unsatisfactory. A comparison of these results with those given in part 3 of this paper is shown in Table LV, page 435.

2. EXPERIMENTAL RESULTS

TABLE LII

Determinations of Density of Alcohol from Experiments XIV and XV

Date	Experiment number	Fraction number	Corrected temperature		Mean corrected temperature t	Apparent weight of sinker in liquid	Air density within balance case	Air buoyancy on weights	True weight of sinker in liquid	Volume of sinker at observed temperature	Density of liquid at observed temperature D_4^t	Density of liquid at 15° D_4^{15}
			Tonnelot No. 4653	Haak No. 2040								
			°C	°C	°C	g	g/ml	g	g	ml		
Dec. 9, 1910	XIV	2	15.158 15.178	15.134 15.167	15.159	62.1524	0.001190	0.0088	62.1436	47.70770	0.793486	0.793621
Do	XIV	4	15.003 14.998	14.992 14.992	14.996	62.1465	.001190	.0088	62.1377	47.70752	.793613	.793610
Dec. 12, 1910	XIV	6	15.058 15.058	15.054 15.057	15.057	62.1487	.001188	.0088	62.1399	47.70759	.793566	.793614
Do	XIV	8	15.058 15.058	15.062 15.067	15.061	62.1488	.001188	.0088	62.1400	47.70759	.793563	.793615
Dec. 28, 1910	XIV	4, 6, and 8 mixed	14.958 14.958	14.944 14.952	14.953	62.1448	.001174	.0087	62.1361	47.70747	.793647	.793607
Jan. 23, 1911	XV	Mixed fractions	15.033 15.018	15.034 15.032	15.029	62.1491	.001203	.0089	62.1402	47.70755	.793560	.793585
Jan. 30, 1911	XV	do	15.093 15.088	15.092 15.092	15.091	62.1507	.001162	.0086	62.1421	47.70762	.793519	.793596
Do	XV	Same sample as preceding	14.948 14.956	14.947 14.952	14.951	62.1452	.001162	.0086	62.1366	47.70747	.793637	.793595
Mean												[1].793603

[1] XIV 2 not included.

Thermometer corrections: No. 4653, +0.°058 C; No. 2040, −0.°008 C. **Mass of sinker No. 7, 99.9990 g.**

TABLE LIII

Density of Alcohol from Experiments XIV and XV

Date	Experiment number	Fraction number	Corrected temperature: Tonnelot No. 4653	Corrected temperature: Haak No. 2040	Mean corrected temperature t	Apparent weight of sinker in liquid	Air density within balance case	Air buoyancy on weights	True weight of sinker in liquid	Volume of sinker at observed temperature	Density of liquid at observed temperature D_4^t	Density of liquid at 25° D_4^{25}
			°C	°C	°C	g	g/ml	g	g	ml		
Jan. 11, 1911.	XIV......	4, 6, and 8 mixed.	24.993 24.993	24.990 24.990	24.992	62.5465	0.001182	0.0088	62.5377	47.71843	0.785049	0.785042
Jan. 23, 1911.	XV......	Mixed fractions..	24.968 24.993	24.992 24.995	24.987	62.5468	.001203	.0090	62.5378	47.71843	.785047	.785036
Jan. 30, 1911.	XV......	.....do...........	25.068 25.073	25.085 25.085	25.078	62.5495	.001162	.0087	62.5408	47.71853	.784982	.785049
Do......	XV.....	Same sample as preceding	25.028 25.030	25.038 25.038	25.034	62.5473	.001162	.0087	62.5386	47.71847	.785029	.785058
Mean.......	....	....	....	....	....	....	....	....	....	....	....	.785046

Thermometer corrections: No. 4653, +0.°008 C; No. 2040, −0.°010 C. **Mass of sinker No. 7, 99.9990 g.**

TABLE LIV

Determination of Densities of Alcohol-Water Mixtures

Designation of mixture	Per cent alcohol by weight	Corrected temperature		Mean corrected temperature t	Apparent weight of sinker in liquid	Air density within balance case	Air buoyancy on weights	Volume of sinker at observed temperature	Density of liquid at observed temperature D_4^t	Density reduced to integral per cent and integral temp. $D_4^{t'}$	Integral per cent	Integral temperature t'
		Tonnelot No. 4653	Haak No. 2040									
		°C	°C	°C	g	g/ml	g	ml				°C
10 E	10. 072	15. 006 15. 008	15. 000 15. 000	15. 004	53. 1123	0. 001181	0. 0075	47. 70752	0. 982954	0. 983053	10	15
10 E	10. 072	25. 056 25. 058	25. 065 25. 065	25. 061	53. 2273	. 001181	. 0075	47. 71851	. 980316	. 980442	10	25
20 E	20. 191	15. 006 15. 006	14. 997 15. 002	15. 003	53. 7074	. 001205	. 0077	47. 70752	. 970482	. 970716	20	15
20 E	20. 191	24. 998 24. 998	24. 990 24. 990	24. 994	53. 9042	. 001205	. 0077	47. 71843	. 966136	. 966407	20	25
20 G	20. 061	14. 923 14. 928	14. 920 14. 924	14. 924	53. 6996	. 001171	. 0075	47. 70743	. 970643	. 970687	20	15
20 G	20. 061	25. 028 25. 033	25. 045 25. 045	25. 038	53. 8967	. 001171	. 0075	47. 71848	. 966288	. 966394	20	25
30 G	30. 244	15. 113 15. 103	15. 107 15. 092	15. 104	54. 3773	. 001179	. 0076	47. 70763	. 956436	. 956891	30	15
30 H	29. 889	14. 996 14. 993	15. 002 15. 002	14. 998	54. 3487	. 001201	. 0078	47. 70752	. 957042	. 956863	30	15
30 H	29. 889	24. 958 24. 983	24. 985 24. 990	24. 979	54. 6324	. 001201	. 0079	47. 71842	. 950880	. 950673	30	25
40 E	39. 970	15. 008 15. 006	14. 997 15. 002	15. 003	55. 2152	. 001182	. 0078	47. 70752	. 938879	. 938822	40	15
40 E	39. 970	24. 908 24. 908	24. 910 24. 912	24. 910	55. 5529	. 001182	. 0078	47. 71834	. 931589	. 931460	40	25
50 E	49. 879	14. 958 14. 958	14. 972 14. 972	14. 965	56. 2084	. 001200	. 0080	47. 70748	. 918066	. 917773	50	15
50 E	49. 879	25. 053 25. 053	25. 070 25. 070	25. 062	56. 5797	. 001200	. 0081	47. 71851	. 910074	. 909853	50	25

TABLE LIV—Continued

Designation of mixture	Per cent alcohol by weight	Corrected temperature		Mean corrected temperature t	Apparent weight of sinker in liquid	Air density within balance case	Air buoyancy on weights	Volume of sinker at observed temperature	Density of liquid at observed temperature D_4^t	Density reduced to integral per cent and integral temp. $D_4^{t'}$	Integral per cent	Integral temperature t'
		Tonnelot No. 4653	Haak No. 2040									
		°C	°C	°C	g	g/ml	g	ml				°C
60 E	60.197	15.038 15.043	15.042 15.042	15.041	57.3207	.001203	.0082	47.70756	.894753	.895239	60	15
60 E	60.197	25.033 25.033	25.048 25.050	25.041	57.7052	.001203	.0083	47.71848	.886493	.886985	60	25
70 E	70.131	15.048 15.053	15.047 15.052	15.050	58.4304	.001164	.0081	47.70758	.871490	.871842	70	15
70 E	70.131	24.908 24.908	24.012 24.012	24.010	58.8196	.001164	.0081	47.71834	.863138	.863374	70	25
70 F	69.957	15.018 15.013	15.017 15.017	15.016	58.4074	.001165	.0081	47.70754	.871973	.871884	70	15
70 F	69.957	24.908 24.933	24.928 24.940	24.927	58.7984	.001165	.0082	47.71836	.863584	.863418	70	25
80 E	80.016	15.053	15.060	15.056	59.5683	.001171	.0083	47.70759	.847643	.847729	80	15
80 E	80.016	25.028 25.028	25.048 25.045	25.038	59.9703	.001171	.0084	47.71848	.839027	.839099	80	25
90 E	89.980	14.858 14.858	14.877 14.872	14.866	60.7707	.001182	.0086	47.70738	.822449	.822281	90	15
90 E	89.980	25.008 25.008	25.025 25.025	25.016	61.1818	.001182	.0086	47.71846	.813643	.813604	90	25
100 (mean)	100.000	....	....	....	....	....	....	....	....	.79360	100	15
100 (mean)	100.000	....	....	....	....	....	....	....	....	.78505	100	25

Thermometer corrections: Tonnelot No. 4653, +C°058 C at 15°; +0°008 at 25° C; Haak No. 2040, −0°008 C at 15°; −0°010 at 25°.
Mass of sinker No. 7, 99.9990 g.

TABLE LV

A Comparison of Results

Per cent alcohol by weight	$D\frac{15°}{4°}C$ Osborne	$D\frac{15°}{4°}C$ Bearce	(O−B) difference ×10⁵	$D\frac{25°}{4°}C$ Osborne	$D\frac{25°}{4°}C$ Bearce.	(O−B) difference ×10⁵
0	0.99913	0.99913	....	0.99708	0.99708	....
10	.98304	.98305	−1	.98043	.98044	−1
20	.97069	.97070	−1	.96639	.96640	−1
30	.95686	.95688	−2	.95067	.95067	0
40	.93883	.93882	+1	.93148	.93146	+2
50	.91776	.91777	−1	.90985	.90985	0
60	.89523	.89524	−1	.88699	.88698	+1
70	.87187	.87186	+1	.86340	.86340	0
80	.84772	.84773	−1	.83911	.83910	+1
90	.82228	.82228	0	.81362	.81360	+2
100	.79360	.79360	0	.78506	.78505	+1

PART 5

BIBLIOGRAPHY

By E. C. McKelvy

VIII. BIBLIOGRAPHY OF THE LITERATURE ON ALCOHOL AND ALCOHOLOMETRY

This bibliography has been compiled to meet the need of workers in the field of alcoholometry and all those interested in the physical properties and purification of the alcohols. It is hoped that the field has been covered reasonably completely. Especial attention has been given to completeness with respect to the purification and physical properties of ethyl alcohol and the points discussed in the present paper. It is considered that practically every physical property has a possible application in alcoholometry and in the tests that go to show the existence of a chemically pure substance. The three factors most important in the choosing of a physical constant for determining the composition of alcohol-water mixtures, or any other binary mixture, are, first, sensitiveness, determined by the rate of change of the given constant with change in composition; second, accuracy of the determination of the physical constant; third, ease and range of applicability. The first, though depending somewhat on the second and third factors, is more or less fixed, being essentially dependent on the nature of the components. The second and third factors depend largely on the state of experimental physical science, and consequently change as science progresses. The study of the relation between physical constants and composition in the binary mixture ethyl alcohol-water, in order to get light on the first factor above mentioned, has been taken up thoroughly for only a few constants. The density and thermal expansion have been studied most extensively because of their early application to alcoholometry. In the determination of the physical constants of pure ethyl alcohol, as a rule, little attention has been paid to the possible water content and its effect. A critical analysis of the results already obtained on other constants besides those above mentioned and the redetermination of many of them are contemplated at this Bureau. The compilation of this bibliography is a preliminary step in that direction.

No attempt has been made to cover the more technological parts of the subject or the chemistry of alcoholic fermentations. Acknowledgment is made of the valuable help given by Dr. W. Bein, of the "Kaiserliche Normal-Eichungs Kommission," Berlin, in the preparation of this part of the work.

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Each reference is made up, where the complete information is available, of the name of author or authors, the journal in which presented, the extent of the article, and the year in which published except where the chronological arrangement shows that information. The references of special interest with respect to the work of this paper are provided with an asterisk. Special parts of extensive articles are indicated by the page number. Notices of the abstracts are also included in the majority of cases.

The references are arranged chronologically by years and alphabetically within the year. They are numbered consecutively. The accompanying numbers in italics refer to the decimal classification of the subject matter and show the subjects treated of in the article in a much more complete manner than the title.

The abbreviations are, with few exceptions, those used by Chemical Abstracts, published by the American Chemical Society. C. B. has been used to indicate "Chemisches Zentralblatt" and J. B. the "Jahresberichte über die Fortschritte der Chemie und verwandter Teile anderer Wissenschaften."

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2. DECIMAL CLASSIFICATION OF SUBJECTS

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14 **Synthesis** 222, 223, 224, 230, 233, 262, 276, 278, 867, 872, 935, 965, 969, 983, 1008, 1018, 1038, 1070, 1080 1165, 1247, 1263, 1286, 1301.

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16 **Alcoholic fermentation** 25, 260, 323, 1036, 1068, 1079, 1170.

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22221 **Change with Temperature. Thermal Expansion** 2, 4, 5, 26, 46, 47, 52, 75, 84, 92, 93, 137, 154, 172, 207, 220, 237, 247, 305, 326, 347, 378, 400, 417, 420, 429, 438, 445, 468,484, 496, 527, 549, 564, 607, 645, 684, 717, 755, 797, 933, 1033, 1087, 1109, 1168, 1211, 1255, 1367, 1376.

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2225 **Surface Tension** 61, 91, 146, 157, 158, 190, 192, 237, 240, 267, 312, 332, 352, 393, 451, 463, 470, 479, 480, 481, 482, 496, 509, 532, 553, 606, 629, 644, 662, 672, 673, 818, 896, 961, 966, 1108, 1113, 1137, 1159, 1211, 1289, 1292, 1330, 1350, 1365.
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MISCELLANEOUS

International Metric System (chart).
Table of the Equivalents of Customary and Metric Weights and Measures.
The International Metric System of Weights and Measures. (Pamphlet.)
First Conference on the Weights and Measures of the United States.
Second Annual Conference on the Weights and Measures of the United States.
Fourth Annual Conference on the Weights and Measures of the United States.
Fifth Annual Conference on the Weights and Measures of the United States.
Sixth Annual Conference on the Weights and Measures of the United States.
The National Bureau of Standards (descriptive pamphlet).

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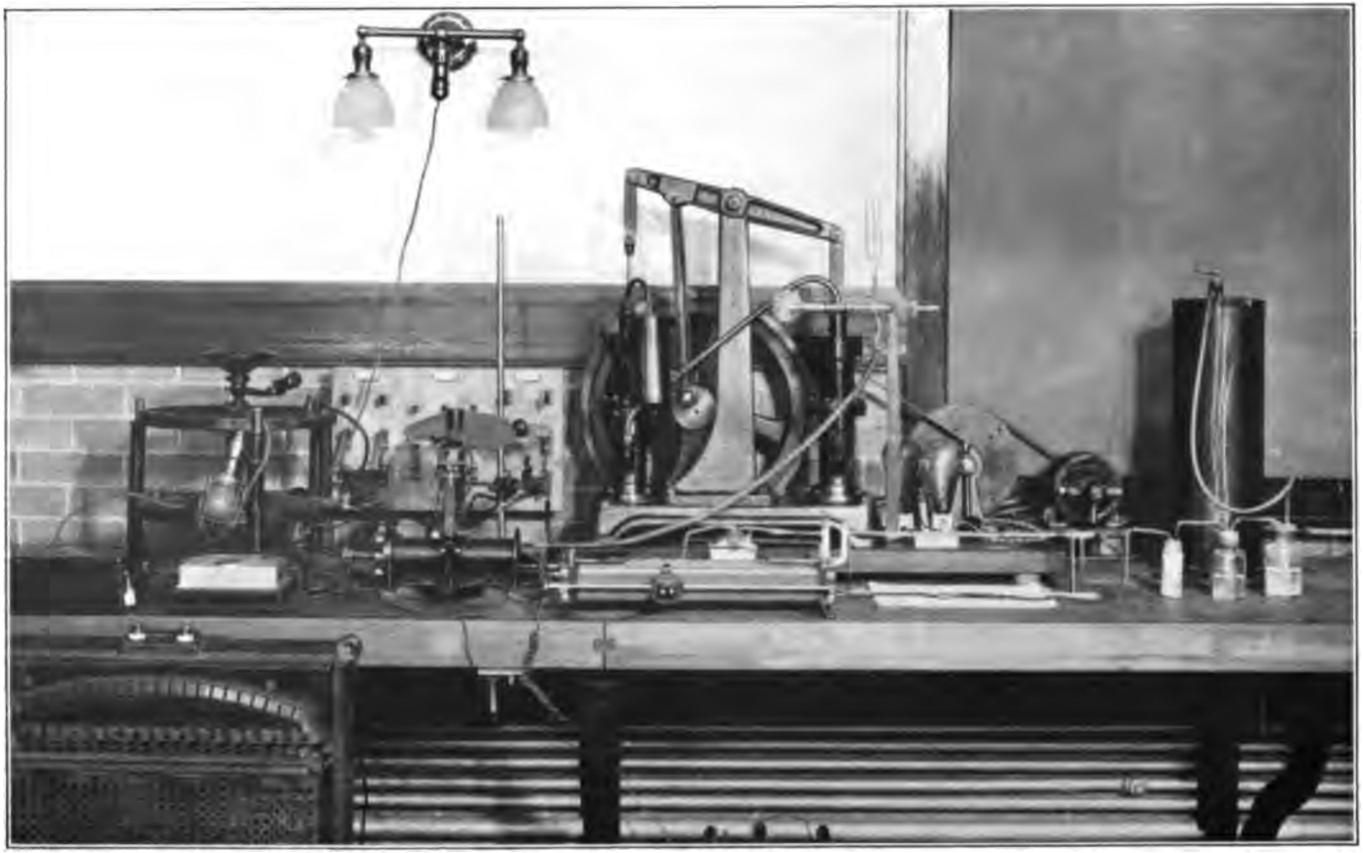

Fig. 1.—*View of the micropyrometer and apparatus*

A MICROPYROMETER

By George K. Burgess

Some time ago a method was described [1] suitable for the rapid estimation of the melting points of minute specimens—as fine as 0.001 milligrams or less. A microscope and an optical pyrometer were sighted through a window of mica, or of plate glass (in case of melts in vacuo), simultaneously on an inclosed metallic strip, such as platinum, heated electrically, and upon which was placed the specimen to be melted.

Evidently this apparatus may be simplified by combining microscope and pyrometer into a single instrument, thus permitting a single observer to watch the melting and measure its temperature. This is effected by mounting within the Huyghens eyepiece of an ordinary microscope a small incandescent lamp, which is in series with a rheostat and ammeter. The tip of the filament of the lamp is set to the same brightness as the platinum strip viewed from above at the instant of melting of the metallic or other specimen on which the microscope is focused. The eye of the observer, therefore, sees the specimen, the platinum strip, and the lamp filament all in focus at once, and the current through the lamp is taken as a measure of the temperature of the strip as in the Morse or Holborn-Kurlbaum pyrometer. In practice, the observer with one hand raises the temperature of the platinum strip by increasing the electric current through it by means of a fine-step rheostat and with the other hand adjusts the rheostat in the pyrometer circuit so as to continuously match in brightness the lamp filament and platinum strip. The eyepiece is furnished with a piece of monochromatic glass, such as Jena red filter No. F 4512. For temperatures above which the lamp should not be burned, say

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[1] G. K. Burgess: Melting Points of the Iron Group Elements by a New Radiation Method, Bull. Bureau of Standards, 3, p. 345; 1907.

1400° C, an absorption glass is placed between the microscope objective and furnace window. The inside of the metallic container or furnace should be blackened to prevent undesirable reflections of light from the walls.

The calibration of the pyrometer as sighted upon the platinum strip in the furnace may be made in two ways. The first, which was the only method available when the earlier form of this apparatus was brought out, due to the dearth of well-known fixed points in the temperature range studied, consists in calibrating the pyrometer in the customary manner and then applying the corrections at the temperatures of melting for the emissivity of platinum, furnace atmosphere, and window, and for the surface tension of the melting specimens when necessary.

The second method, which appears to be the more accurate and also more convenient, consists in observing the lamp currents at the known melting points of two or more pure substances, such as gold, nickel, cobalt, and palladium, and from the equation expressing the relation between temperature and current in lamp the temperature of melting of any specimen may be computed. For not too great temperature intervals we may use the equation $\log c = a + b \log t$, which permits calibration with two fixed points only.

This second method of calibration has the further advantage that, for materials of approximately the same general properties, the error of method is eliminated. Thus, in the case of metals which alloy with platinum, the effects of alloying, conductivity, and of surface tension enter into the calibration as well as into the determination of the unknown melting point, so that any outstanding error will be but a residual one. In the case of substances of dissimilar properties, such as salts and metals, this apparatus must be used with caution, for, in general, a calibration made in terms of the metal melting points, for example, will not serve for the exact determination of the melting points of salts.

The precision of the method is dependent mainly upon the character of the melting of the substances observed. With metals such as gold and nickel, which melt very sharply, a precision of 1° or 2° C is obtainable.

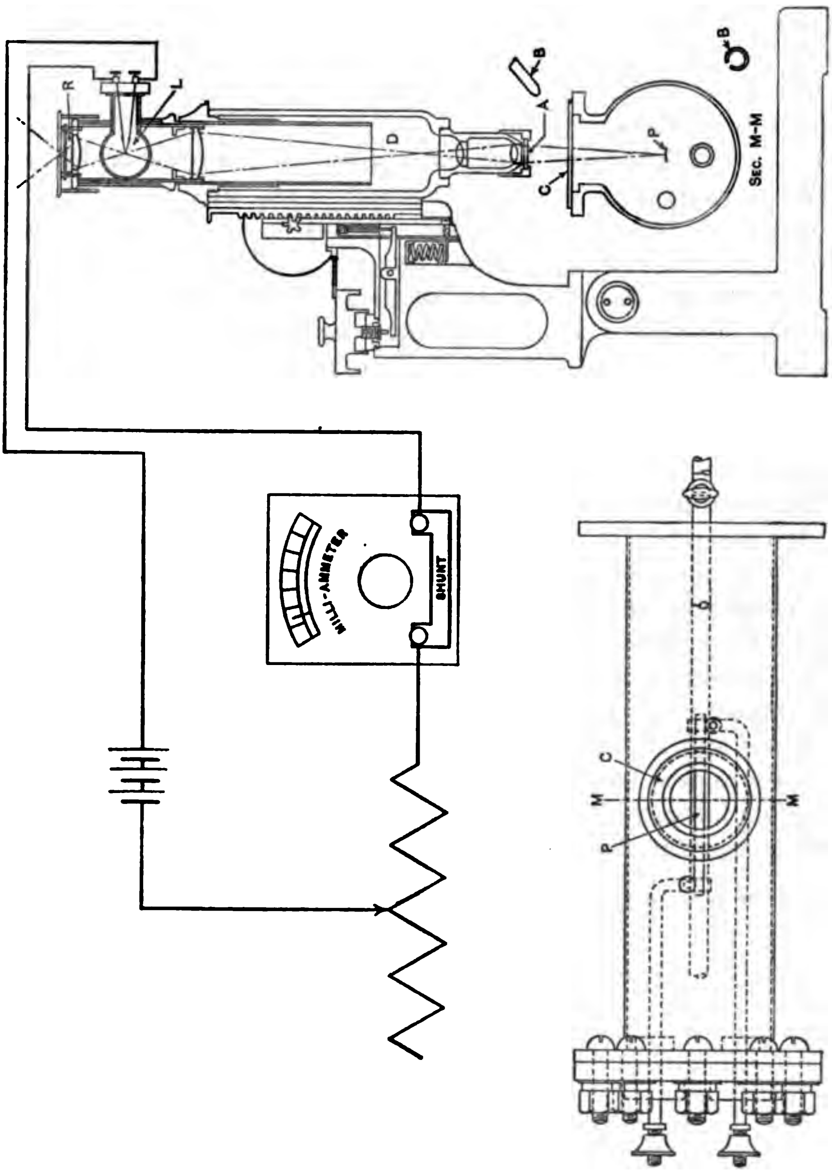

Fig. 2

The apparatus as constructed at the Bureau of Standards, largely from suggestions due to Messrs. Crowe and Foote, of this Bureau, is shown in Fig. 2, in which L is the pyrometer lamp, R the monochromatic glass, A the absorption glass, P the platinum strip carrying the specimen, C the furnace window, B an air blast for cooling the surface.

Fig. 1 is a photograph of the apparatus arranged for taking melting points in a hydrogen vacuum. The microscope has a Bausch and Lomb 48-mm single achromatic lens and 6.4 x eyepiece and gives sufficiently good definition and magnification and a large enough field of view for melting point observations. The working distance of the objective may be increased, if desired, by the device employed by Robin [2] of inserting a biconcave lens at D, slightly back of the focus of the objective. This necessitates lengthening considerably the draw-tube and reduces the area sighted upon.

The micropyrometer may, of course, be used for the estimation of temperatures of incandescent surfaces simultaneously with their examination, and thus becomes a useful instrument in metallographic and microchemical and physical investigations at high temperatures.

The apparatus is being used at the Bureau of Standards for the determination of melting points and emissivities of the refractory elements and alloys, and the author will be glad to receive pure samples (a few hundredths milligram), particularly of the rarer elements for such determinations.

WASHINGTON, December 9, 1912.

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[2] F. Robin: Microscope à longue portée etc., Bull de la Société d'Encouragement, 118; p. 204; 1912.

A SIMPLIFIED FORMULA FOR THE CHANGE IN ORDER OF INTERFERENCE DUE TO CHANGES IN TEMPERATURE AND PRESSURE OF AIR

By Irwin G. Priest

A change in the density of the air between two interferometer mirrors, as in the Fabry-Perot interferometer or the Fizeau apparatus for expansion coefficients, by altering the refractive index, causes a change in the optical difference of path and in the order of interference. The change in density may be occasioned by either a change in the temperature or in the pressure, and the relation holding between the refractive index (μ) and the density (d) is expressed by Gladstone and Dale's law:

$$\frac{\mu-1}{d}=\text{constant}.$$

In the interference method for expansion coefficients a correction must therefore be applied to the observed change in the order of interference, to take account of any change in the density of the air. The following formula for this correction was published by Pulfrich in 1893:[1]

$$K=l(t_2-t_1)\frac{b_1}{760}\cdot\frac{1}{1+\alpha t_1}\cdot\frac{1}{1+\alpha t_2}\left[\frac{2(\mu-1)\alpha}{\lambda}\right]$$
$$-l(b_2-b_1)\cdot\frac{1}{1+\alpha t_2}\left[\frac{2(\mu-1)}{760\lambda}\right]$$

Where:

l = distance between mirrors.
t_1 = lower temperature (in degrees centigrade).
t_2 = upper temperature.
b_1 = pressure in mm of mercury at temperature t_1.
b_2 = pressure in mm of mercury at temperature t_2.
α = expansion coefficient of air.
μ = refractive index at 0°, 760.
λ = wave length.

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[1] Zs. für Instrk., 18, p. 456. The sign of the expression in the original paper is reversed if the expression is to represent the correction, not the error.

The above formula has been used by Reimerdes, Randall, and Minchin.

Some months ago I derived independently the following much simpler formula for the same correction:

$$K=\left(\frac{b_1}{1+\alpha t_1}-\frac{b_2}{1+\alpha t_2}\right)l\left[\frac{\mu-1}{380\lambda}\right]$$

After using this formula at the Bureau of Standards for several months, I noticed that the Pulfrich formula could be reduced to it by simple algebraic transformations.

The part of the expression in square brackets is constant for constant wave length. The value of $\frac{1}{1+\alpha t}$ may be obtained from the Landolt-Börnstein tables or from a graph constructed for the temperatures most frequently used. Assuming the use of the same reference tables in each case, and that the constant parts of each expression have been evaluated, the operations required to obtain a numerical value are as follows:

	Subtractions	Multiplications	Divisions
Pulfrich form	3	8	1
New form	1	4	0

The following is the derivation of the new formula:

In addition to above symbols, let μ_1, μ_2; n_1, n_2; d_1, d_2 represent refractive indices, orders of interference, and densities of air at temperatures t_1 and t_2, respectively. Let λ be the wave length in vacuo.

Then

$$n_1=\frac{2\mu_1 l}{\lambda} \qquad (1)$$

$$n_2=\frac{2\mu_2 l}{\lambda} \qquad (2)$$

$$n_2-n_1=\frac{2l(\mu_2-\mu_1)}{\lambda} \qquad (3)$$

By Gladstone and Dale's law

$$\mu_2 = 1 + c\,d_2 \tag{4}$$

$$\mu_1 = 1 + c\,d_1 \tag{5}$$

Where c = Gladstone and Dale constant. But by the simple gas laws,

$$d_2 = \frac{d_0 b_2}{(1 + \alpha t_2)\ 760} \tag{6}$$

and

$$d_1 = \frac{d_0 b_1}{(1 + \alpha t_1)\ 760} \tag{7}$$

Where d_0 = density of air at 0° and 760 mm. Representing c by $\frac{\mu - 1}{d_0}$, substituting (7) and (6) in (5) and (4); and (5) and (4) in (3), and simplifying we find

$$n_2 - n_1 = \frac{l(\mu - 1)}{380\lambda}\left(\cdot\frac{b_2}{1 + \alpha t_2} - \frac{b_1}{1 + \alpha t_1}\right)$$

This is the change in the order of interference as the temperature increases from t_1 to t_2 and the pressure changes from b_1 to b_2 (increase or decrease). The correction is the above expression with sign reversed, thus:

$$K = \left(\frac{b_1}{1 + \alpha t_1} - \frac{b_2}{1 + \alpha t_2}\right) l \left[\frac{\mu - 1}{380\lambda}\right]$$

WASHINGTON, October, 1912.

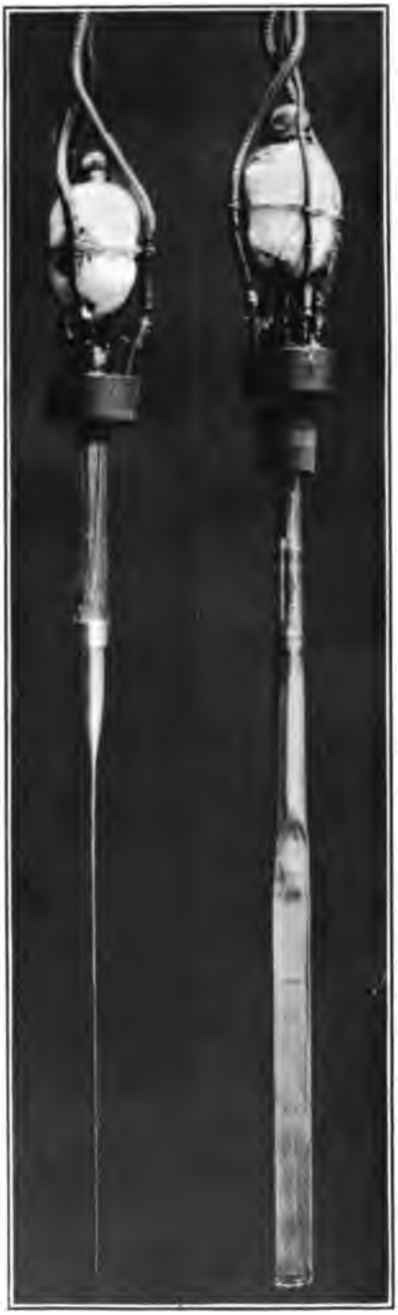

Fig. 1. –*New form of calorimetric resistance thermometers.*

NEW CALORIMETRIC RESISTANCE THERMOMETERS

By H. C. Dickinson and E. F. Mueller

Since the publication of the paper "Calorimetric Resistance Thermometers and the Transition Temperature of Sodium Sulphate"[1] improvements made in the type of resistance thermometer there described have changed it from a special laboratory instrument into one of extensive application for precision measurements of temperature in the interval −180° to +180°, or, with slight modifications, up to 500°[2]. Since these instruments have now been put on the market and a considerable number are in use, a description of the newer form may be of interest.

This paper is intended merely as a general description and not as a set of working directions. Information as to methods of construction and necessary precautions will be furnished to anyone desiring to make thermometers of this type.

The thermometers described in the earlier paper were somewhat limited in their applicability because of the presence of solder in the sheath, of hard rubber at the upper end of the sheath, and of a wax joint between the metal and the hard-rubber head. The wire used was 0.02 mm in diameter, which limited the sensibility by reducing the allowable measuring current, thus rendering necessary the use of very sensitive galvanometers.

The type of thermometer now in use is the result of a gradual development in the course of which a number of thermometers have been constructed. Two of the new thermometers are shown in Fig. 1 and details of construction in Fig. 2. The changes made have led to a greater ease of construction, robustness, reliability, and general utility.

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[1] This Bulletin, 3, p. 640, Reprint No. 68.

[2] Up to this time these instruments have actually been used only between the limits of −180° and +150°.

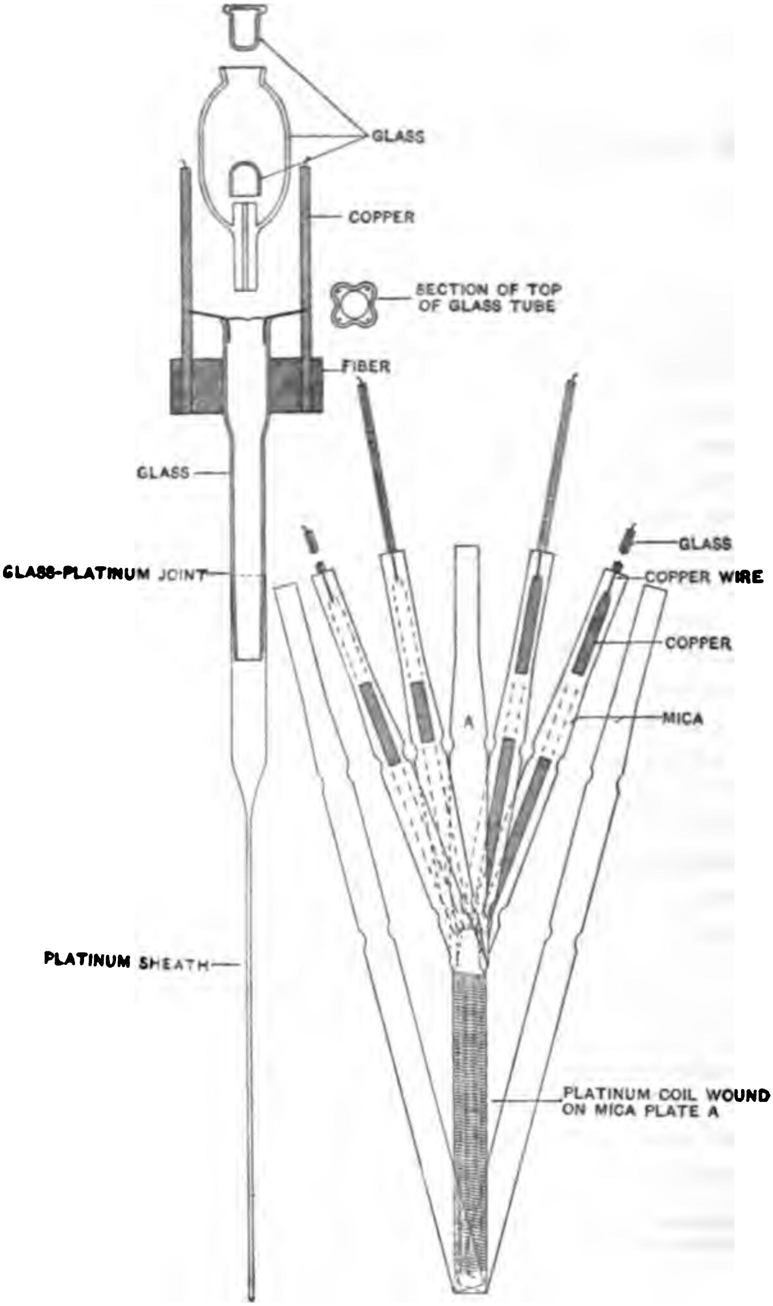

Fig. 2.—*Diagrammatic sketch of parts of thermometer, separated to show construction.*

Coil.—The coil is of the purest Heraeus platinum wire 0.1 mm in diameter, a length of about 2.2 meters being wound in a flat bifilar coil about 8 cm long and 7 mm broad, on one end of a mica strip, which is about 18 cm long, and 0.2 mm. thick.

The turns of wire are held in place by notches in the sides of the mica strip and are spaced about 14 turns to the centimeter. The coil is insulated from the surrounding sheath by strips of mica somewhat wider and thinner than that on which the coil is wound. Before winding, the wire is annealed by heating to a high temperature, 1000° to 1200° C by passing an electric current through it. After winding and attaching the leads, i. e., after the coil is so far completed as not to require further handling, it is carefully washed in distilled water to remove all traces of hygroscopic salts and is then heated to a bright red by means of an electric current to drive off all volatile matter, and to reanneal the wire.

Leads.—Three forms of connection are adapted to use respectively with (a) a shunted bridge only; (b) a shunted bridge or a slide-wire bridge; (c) a shunted bridge, a Kelvin bridge, a differential galvanometer, or a potentiometer. The connections are made as shown in Fig. 3. In all three types the effect of lead resistance is eliminated.

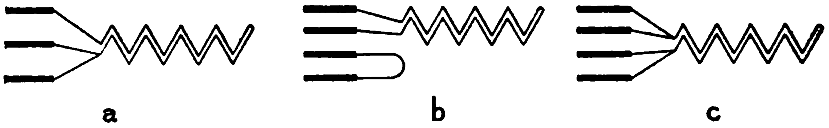

Fig. 3

The leads for any of these forms are made of thin strips of No. 36 B. & S. gage (0.13 mm) copper 2 to 3 mm wide; but in a single thermometer all are made alike. In the forms (a) and (c) the copper lead is separated from the branch point by from 15 to 20 mm of the 0.1-mm platinum wire. In the form (b) the compensating loop is closed by a piece of this wire 3 or 4 cm long. All platinum joints are made by fusing with an arc, using a pure graphite electrode, while the copper platinum joints are made either by welding or with silver, using borax as a flux. The flat copper strips extend to just beyond the mica strips, where they are silver-soldered to No. 20 copper wires, which are threaded through glass tubes. If suitable rolls are available, it is preferable to roll down the wires at the ends to take the place of the copper strips.

Sheath.—The sheaths are made of thin drawn silver or (preferably) platinum tubes 7 mm in diameter, 15 to 18 cm long, and of about 0.12 mm wall thickness for the platinum and up to 0.2 mm for the silver. These tubes are partially flattened, as shown in Fig. 1, and after the coil is inserted are closed at the ends by fusing with an arc, and pressed down onto the coil.

Heads.—The heads are made entirely of glass and consist of four pieces, as shown in Fig. 2—the stem, drying capsule, and two small caps. The stems are usually attached to the metal cases by platinizing the glass, which is just large enough to slip into the metal tube, and then soldering the glass and metal together with ordinary soft solder. As this solder melts at about 190° C, thermometers to be used above this temperature have the case made of platinum, which is fused directly to the glass. This method requires a rather large joint between the glass and platinum. The glass must be of special composition (such as Jena 397^{III}) and the work carefully done to avoid breaking at this point.

The upper part of this tube is shaped to provide grooves for the lead wires, which are brought out between the tube and the stem of the drying capsule. The drying capsule is sealed in with Khotinski cement, the wires passing out through this cement.

The drying capsule is about half filled with asbestos wool, the small inside glass cap serving to prevent loose particles from dropping into the tube below. The rest of the capsule is filled with phosphorus pentoxide. When the small upper cap is cemented on, the thermometer is kept warm to prevent the internal pressure becoming larger than one atmosphere when the thermometer is subsequently used at the higher temperatures.

Outside leads.—The coil leads are soldered to pins or small copper tubes held in a fiber collar which is cemented to the glass stem. To these pins or tubes the flexible leads of No. 18 or No. 20 silk-covered lamp cord are attached. These leads are as nearly as possible alike, both as to length and total resistance, and preferably not more than 2 or 3 m long. The battery leads in forms (a) and (c) may be of No. 22 wire. These wires are so protected at the soldered joints as to prevent sharp bending. This may be accomplished by threading the wire through the copper tubes and making the soldered joint at the lower end.

Essential Features.—It is worth while to emphasize some of the points to which attention had to be given to make thermometers of this type successful. Some of these are essential to the success of any type of resistance thermometer and have been duly emphasized in many other publications. The more important are:

1. Securing and maintaining a *high insulation resistance* by taking care when making up the coils to secure absolute cleanliness and freedom from foreign matter and then sealing a drying agent inside the thermometer.

2. Mounting in such a way as to avoid subjecting the resistance wire to strains.

3. Providing close contact between the wire, insulating material, and sheath (the total thickness is less than 1 mm), reducing the lag, and thereby allowing the use of a relatively large measuring current.

4. Using the compensating leads to eliminate not only the effect of variable resistance of the thermometer leads due to varying temperatures, but also the effect of thermal conduction in these leads by having a loop of the same wire which is used for the coil attached to the compensating leads.

5. *Eliminating thermoelectric troubles* due to copper-platinum junctions by having all such junctions down in the sheath close together, where they will all be immersed in the bath the temperature of which is to be measured.

All of these features, with the possible exception of the drying agent, are essential to this type of thermometer.

Constants of the Thermometers.—The thermometers made, up to the present time, have been constructed to have a resistance such that the change between 0° and 100° C is very nearly 10 ohms, which requires a resistance of about 25.6 ohms at a temperature of 0° C. Computation of temperatures, and particularly of temperature differences, is very much facilitated by this means, since nearly all computations can be made with a 10-inch slide rule.

If the thermometer is to be used solely for calorimetric work, a resistance of 25.3 ohms at 0° C is convenient, giving about 0.1 ohm per degree at 20°.

The wire used in these thermometers being of the purest platinum obtainable, the fundamental coefficient is 0.00391 as against 0.00336 for the wire used in the older type. The value of δ (in the Callendar formula) is for these thermometers about 1.47 when computed from observations at 0°, 50°, and 100° or at 0°, 32°.384, and 100° as against 1.55 for the older thermometers.

Measuring Current.—The current generally used with these thermometers is 5 to 6 milliamperes. This causes a rise of temperature of the wire above that of a water bath in which the thermometer is immersed, of the order of 0°.002, varying somewhat in individual thermometers. This amount of heating is entirely permissible when measurements are to be made to 0°.0001, since the current may change by over 2 per cent without producing a change of 0°.0001. In fact, the measuring current is limited, not by the amount of the heating but by the fact that the bridge is unbalanced with the current off, so that closing the battery circuit causes a throw of the galvanometer. It is the desirability of limiting the heating so that equilibrium, within the limit of reading, shall be established in a time not much longer than the period of the galvanometer swing, that fixes the convenient limit to the measuring current.

Performance.—The behavior of these thermometers has been very satisfactory, although some have proven a little more constant than others. The best of them have shown variations of less than 0°.001, in melting ice from time to time, during two years or more; what proportion of this observed change is attributable to the thermometer and what to the resistance coils of the bridge and the standard of reference or to the actual changes in the temperature of the ice bath is uncertain. Such variations do not necessarily produce any such error in the measurement of temperature changes. In fact, there is nothing to indicate that these thermometers are unreliable for such measurements even to the extent of 0°.0001. The thermometers mentioned were of the 3-lead (Fig. 3, *a*) type, so that the variations referred to include variations in the stranded leads. Inasmuch as this has been considered a serious source of error,[3] it is well to call particular attention to this point. With care in handling leads the variations have never exceeded 0.0001 ohm.

Defects.—The variations in the resistance of the stranded leads may become serious if they are carelessly handled so as to break one or more strands. This will manifest itself by erratic changes in the apparent resistance when the thermometer is at a constant temperature. Other causes of variation such as strains in the wire will usually be detected and should be eliminated during the original calibration.

The presence of moisture in the thermometer, due to a leak or to exhaustion of the drying material, may occur. The resulting phenomena are very characteristic and easily recognized. If the bridge, with the thermometer in circuit and galvanometer circuit closed and a key in the battery circuit, is balanced by adjusting resistance with the battery key closed, then on opening the battery circuit there will be a large deflection of the galvanometer, which gradually diminishes and on closing it again, another large deflection in the opposite direction. The latter slowly diminishes if the circuit is kept closed. This phenomenon is readily distinguished from that due to the use of an excessive measuring current, by the absence of the galvanometer deflection in the latter case, when the battery circuit is opened.

The presence of moisture also reduces the insulation resistance between the coil and sheath. This insulation resistance is easily tested and should exceed 200 megohms.

Difference Formula.—The ordinary Callendar equations are very convenient for most computations, but for computation of temperature differences the calculation may be made much more simple by the use of a single factor.

The Callendar equations are

$$pt=\frac{R_t-R_o}{R_{100}-R_o}\,100,\text{ or since } R_{100}-R_o=R_o\,(100c)$$

$$pt=\frac{R_t-R_o}{R_oc} \qquad (1)$$

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[3] F. E. Smith: Phil. Mag. [VI], 24, p. 542; 1912.

and

$$t - pt = \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} \tag{2}$$

These two equations are easily combined into a single one

$$R_t = R_0(1 + \alpha t + \beta t^2) \text{ where} \tag{3}$$

$$\alpha = c\left(1 + \frac{\delta}{100}\right) \text{ and } \beta = -\frac{c\delta}{100^2}$$

Suppose the difference of two temperatures t_1 and t_2 is to be computed from the corresponding values R_1 and R_2 we have,

$$R_2 = R_0\,(1 + \alpha t_2 + \beta t_2^2)$$

$$R_1 = R_0\,(1 + \alpha t_1 + \beta t_1^2)$$

$$R_2 - R_1 = R_0\,[\alpha(t_2 - t_1) + \beta\,(t_2 - t_1)\,(t_2 + t_1)]$$

$$= R_0\,(t_2 - t_1)\,(\alpha + 2\,\beta\,T)$$

$$\text{Where } T = \frac{t_2 + t_1}{2} = \text{mean } t$$

$$\text{Then } t_2 - t_1 = \frac{1}{R_0(\alpha + 2\,\beta T)}\,(R_2 - R_1)$$

or

$$\Delta t = \frac{1}{R_0\,(\alpha + 2\beta\,T)}\,\Delta\,R \tag{4}$$

This is of the same form as the formula obtained bv differentiation

$$\delta t = \frac{1}{R_0\,(\alpha + 2\,\beta t)}\,\delta R$$

and the condition that the formula hold for finite differences is that T be the mean of the two temperatures, t_1 and t_2, the difference of which is to be measured.

The formula may be rewritten in terms of the constants used in the Callendar formula

$$\Delta t = \frac{100}{(R_{100} - R_0)\left(1 + \frac{\delta}{100} - \frac{2\delta T}{100^2}\right)}\Delta\,R \tag{5}$$

From (5) a table of factors may be computed as follows: A series of values of $\bar{R}$, the mean of R_1 and R_2 is assumed, the corresponding values of T are then computed and substituted in the formula. This table is then used as an interpolation table to find Δt when R_1 and R_2 are given.

The computation for a thermometer which has the constants $R_o = 25.3012$, $R_{100} - R_o = 9.8902$, $\delta = 1.47$ is given in the table below.

R	pt	T	$\frac{100}{R_{100}-R_o}$	$1+\frac{\delta}{100}-\frac{2\delta T}{100^2}$	Factor
26.8	15.154	14.97	10.1110	1.01030	10.0079
9	16.165	15.97	10.1110	01000	109
27.0	17.176	16.97	10.1110	00971	138
1	18.188	17.97	10.1110	941	168
2	19.199	18.97	10.1110	912	197
3	20.210	19.97	10.1110	882	226
4	21.221	20.98	10.1110	853	255
27.5	22.232	21.98	10.1110	823	285
6	23.243	22.98	10.1110	794	314
7	24.254	23.99	10.1110	765	343
8	25.265	24.99	10.1110	735	372

As the constants from which the table is derived warrant an accuracy of only 1 in 10 000, the factors in the last column would in practice be carried out only to the third decimal place.

When using such a thermometer, e. g., in a calorimetric measurement, all calculations, such as that for cooling correction, etc., are made in terms of resistance instead of temperature, and the final value $R_2 - R_1$ for the change in resistance is multiplied by the appropriate factor corresponding to $\overline{R} = \frac{R_2 + R_1}{2}$, to find $t_2 - t_1$.

It appears that an error due to this method of calculation may be introduced, since the factor which should be used is that corresponding to $T = \frac{t_2 + t_1}{2}$, while the one actually used is that corresponding to the t defined by $\overline{R} = R_0\ (1 + \alpha t + \beta t^2)$. It is easily shown, however, that the error is insignificant. If we write $t_2 - t_1 = \tau$, then a simple calculation shows that

$$T - t = \frac{-\beta\tau^2}{4\{\alpha + \beta(T + t)\}} = \frac{-\beta\tau^2}{4(\alpha + 2\beta T)} \text{ approximately.}$$

If $\tau = 10°$ and $T = 0°$, then from the above $T - t = 0\overset{\circ}{.}0036$, the result depending only in a minor degree on T. From the table of factors it is seen that the factor changes by about 30 parts in 100 000 per degree, so that the error for a 10° rise amounts to about 1 in 1 000 000. Since the error increases as the square of the temperature difference, it follows that the table can be used for differences up to 30° before the error becomes as large as 1 in 100 000.

Summary.—An improved form of calorimetric resistance thermometer is described and some points of interest in connection with its use are given.

A difference formula for simplifying calorimetric computations is given and its applicability shown.

WASHINGTON, January 1, 1913.

THE SILVER VOLTAMETER—PART III

SECOND SERIES OF QUANTITATIVE EXPERIMENTS AND THE PREPARATION AND TESTING OF SILVER NITRATE

By E. B. Rosa, G. W. Vinal, and A. S. McDaniel

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I. QUANTITATIVE EXPERIMENTS, SECOND SERIES

A. INTRODUCTION

The second series of quantitative experiments began on December 17, 1909, after several months spent in the work described in the second paper.[1] The first series had been chiefly concerned with the investigation of the filter paper voltameter, and, together with the qualitative investigations, had demonstrated the action of filter paper on the silver nitrate to be so considerable as to make this form of voltameter unreliable for work of high precision. In the present series of experiments attention was directed chiefly to the porous pot and nonseptum forms of voltameters. The apparatus and methods used were similar to those previously employed which have been described in the first paper.[2] Some of the problems studied were the so-called "volume effect," the trouble from anode slime in the Poggendorff form and the cause of used solutions yielding somewhat lower values for the electrochemical equivalent than new solutions when filter paper is excluded.

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[1] This Bulletin, 9, p. 209, Reprint No. 195.

[2] This Bulletin, 9, p. 157, Reprint No. 194.

B. GENERAL TABLE OF RESULTS

Between December 17, 1909, and April 5, 1910, 156 deposits of silver were made, which are recorded in Table 1. In the column giving the electrochemical equivalent of silver the results are expressed in milligrams per coulomb, which is based on the Weston Normal Cell having a voltage of 1.01890 at 25° C, because this is the value which was in use in the United States prior to January 1, 1911. In the subsequent tables the results have been classified according to the form of voltameter in which they were made. In these tables the original figures for the electrochemical equivalent are given, and in addition the voltage of the Weston Normal Cell computed from the weight of deposit, the time, and the electrochemical equivalent of 1.11800 mg. per coulomb as specified by the London Conference of 1908. In doing this, however, a correction of three parts in 100 000 to our electrical standards has been found necessary and has been applied.[3]

The electrolytes are designated as before. "Baker" means $AgNO_3$ from the J. T. Baker Chemical Co., of Phillipsburg, N. J., while "Frankfurt" indicates that the salt was procured from the Gold- und Silber- Scheide- Anstalt of Frankfurt, Germany. In some cases it has been recrystallized by ourselves, in which case this fact is noted.

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[3] Report of the International Technical Committee, p. 26.

TABLE 1

General Table of Quantitative Results for 1910

Date	No.	Bowl	Form	Electrolyte	Time	Current	Deposit	Electro-chemical equivalent	Remarks
1909					sec.	amp.	mg		
Dec. 17	122	95	Richards	Frankfurt 15%	7200.00	0.500424	4097.16	1.11705	Large porous cup
	123	93	Poggendorff	Frankfurt 10%			4102.45	849	Without silk; anode slime on cathode
	124	92	Richards	do			4097.38	711	Large porous cup
	125	26	do	do			97.02	701	Do.
	126	127	Poggendorff	Frankfurt 15%			98.19	733	Without silk
	127	128	do	do			98.41	738	Do.
	128	27	Richards	do			96.93	698	Small porous cup
	129	28	do	do			97.27	707	Coarse porous cup
	130	125	do	do			96.98	700	Small porous cup
	131	126	do	do			97.10	703	Do.
1910									
Jan. 7	132	95	Rayleigh	Baker 10%	2 hours	½ amp.	4098.84		Less filter paper than usual
	133	93	Siphon	do			99.55		Volume of liquid, 500 cc
	134	92	do	do			99.57		Do.
	135	26	Richards	do			98.24		
	136	127	Poggendorff	do			99.31		Without silk
	137	128	do	do			99.26		Do.
	138	27	Richards	do			98.04		
	139	28	do	do			98.74		Coarse porous cup
	140	125	do	do			98.10		
	141	126	do	do			97.97		

13	142	95	Siphon	Frankfurt 10%	2 hours	½ amp.	4097.27		500 cc of electrolyte
	143	93	do	do			97.32		Do.
	144	92	Richards	do			96.59		Large porous cup
	145	27	do	do			96.34		
	146	28	do	do			96.34		
21	147	95	Siphon	Used Frankfurt filtered	2 hours	½ amp.	4149.11		
	148	93	do	do			48.58		Porous cup on cathode end of siphon
	149	92	Richards	do			48.86		Small porous cup
	150	26	do	New Frankfurt filtered			48.76		Large porous cup
	151	127	Poggendorff	Used Frankfurt filtered			48.61		
	152	128	do	New Frankfurt filtered			48.58		Without silk
	153	27	Richards	Used Frankfurt filtered			48.47		Do.
	154	28	do	New Frankfurt filtered			48.34		Coarse porous cup
	155	125	do	Used Baker filtered			46.52		Abnormal
	156	126	Rayleigh	New Frankfurt filtered			50.37		One sheet filter paper
26	157	27	Richards	Frankfurt 10% filtered	7200.90	0.509372	4096.78	1.11687	Pasteur filter No. 1 used
	158	28	do	Frankfurt 10%			97.41	704	Not filtered
	159	125	do	do			97.56	709	Do.
	160	126	do	Frankfurt 10% filtered			96.91	691	Pasteur filter No. 1 used
28	161	27	do	Frankfurt 10%	7199.86	0.509422	4096.97	1.11702	Not filtered
	162	28	do	Frankfurt 10% filtered			96.89	700	Pukal bulb used as filter
	163	125	do	Frankfurt 10%			96.94	701	Not filtered
	164	126	do	Frankfurt 10% filtered			96.93	701	Pukal bulb used as filter
31		27	Asbestos	Frankfurt 10%	2 hours	½ amp.			Asbestos mat disintegrated
	165	28	Richards	do			4163.51		Platinum cathode
		125	Asbestos	do					Asbestos mat disintegrated
	166	126	Richards	do			63.55		Gold cathode
Feb. 3	167	27	do	do	2 hours	½ amp.	4130.93		
	168	28	do	Frankfurt 15%			30.89		
	169	125	do	do			30.84		
	170	126	do	Frankfurt 10%			30.95		

TABLE 1—Continued

General Table of Quantitative Results for 1910—Continued

Date	No.	Bowl	Form	Electrolyte	Time	Current	Deposit	Electro-chemical equivalent	Remarks
					sec.	amp.	mg.		
Feb. 5	171	95	Siphon	Used solution	2 hours	½ amp.	4124.61		Porous cup on anode end; short circuit
	172	93	do	do			33.23		Siphon without porous cup
	173	27	Richards	do			31.24		
	174	28	do	do			27.77		Deposit spoiled
8	175	27	do	Frankfurt 10%	7200.28	0.509438	4097.39	1.11704	
	176	28	do	Used solution			97.09	695	Anode liquid
	177	125	do	Frankfurt 10%			97.38	708	
	178	126	do	Used solution			97.03	694	Do.
10	179	27	do	Frankfurt 10%	7202.50	0.509429	4098.69	1.11707	Not filtered
	180	28	do	Frankfutt 10% filtered			98.30	696	Pasteur filter No. 1 used
	181	125	do	Frankfurt 10%			98.74	708	Not filtered
	182	126	do	Frankfurt 10% filtered			98.23	694	Pasteur filter No. 1 used
12	183	95	Siphon	Frankfurt 10%	2 hours	½ amp.	4105.75		Porous cup over anode end of siphon
	184	93	do	do			05.63		Without porous cup
	185	27	Richards	do			05.04		
	186	28	do	do			05.05		
15	187	27	do	do	7200.38	0.509432	4097.42	1.11704	
	188	28	do	Used solution+added salt			97.43	704	Frankfort salt added to bring concentration to 10%
	189	125	do	do			97.34	702	
	190	126	do	Frankfurt 10%			97.10	696	Silver lost

17	191	27	.....do.........	Used+salt, filtered No. 2........	7200.71	0.509470	4097.84	1.11702	Same electrolyte as No. 188 and 189 filtered through Pasteur filters No. 1 and No. 2 especially cleaned
	192	28	.....do..........	Used+salt, filtered No. 1........			97.63	696	
	193	125	.....do..........	.....do..........................			97.59	695	
	194	126	.....do..........	Used+salt, filtered No. 2........			97.69	698	
19	195	27	.....do..........	Frankfurt 10% filtered...........	7202.76	0.509431	4098.68	1.11702	Electrolyte for two filtered through purified asbestos Filtered and unfiltered agree
	196	28	.....do..........	Frankfurt10% unfiltered........			98.77	704	
	197	125	.....do..........	.....do..........................			98.64	701	
	198	126	.....do..........	Frankfurt 10% filtered...........			98.69	702	
23	199	27	Rayleigh........	Frankfurt 10%..................	7202.90	0.509432	4100.41	1.11746	One sheet of No. 595 paper
	200	28	Richards........	.....do..........................			4098.79	702	
	201	125	.....do..........	.....do..........................			98.62	697	
	202	126	Rayleigh........	.....do..........................			4100.59	751	Do.
25	203	27	Richards........	.....do..........................	7202.27	0.509427	4098.46	1.11704	Neutral electrolyte
	204	28	.....do..........	.....do..........................			98.33	701	Acid 1×10^{-6} present
	205	125	.....do..........	.....do..........................			98.28	699	Do.
	206	126	.....do..........	.....do..........................			98.15	696	Neutral electrolyte
	207	127	Poggendorff.....	.....do..........................			98.35	701	Washed silk used
	208	128	.....do..........	.....do..........................			98.56	707	Do.
Mar. 2	209	95	Siphon...........	.....do..........................			4099.37	1.11756	In parallel both halves
	210	93	.....do..........	.....do..........................			98.99		
	211	27	.....do..........	.....do..........................	First half.		98.83	743	Do.
	212	125	.....do..........	.....do..........................	7200.04	0.509422	98.56		
	213	126	Richards........	.....do..........................	Second half.		97.25	707	In first half only
	214	28	.....do..........	.....do..........................	7200.54	0.509415	97.62	711	In second half only
	215	127	Poggendorff.....	.....do..........................			97.26	707	In first half only; silk used
	216	128	.....do..........	.....do..........................			97.72	713	In second half only; silk used
5	217	95	Siphon...........	.....do..........................			8199.81	1.11774	Double siphon. In both halves
	218	127	Poggendorff.....	.....do..........................	First half.		4097.52	712	With silk. In first half
	219	128	.....do..........	.....do..........................	7200.20	0.509422	8195.93	721	With silk. In both halves
	220	28	Richards........	.....do..........................			4066.81	708	In parallel both halves
	221	125	.....do..........	.....do..........................	Second half.		4128.14		
	222	126	.....do..........	.....do..........................	7200.62	0.509417	4097.30	706	In first half only
	....	27	.....do..........	.....do..........................			....	....	Spoiled; deposit grew through porous cup

TABLE 1—Continued

General Table of Quantitative Results for 1910—Continued

Date	No.	Bowl	Form	Electrolyte	Time	Current	Deposit	Electro-chemical equivalent	Remarks
					sec.	amp.	mg.		
Mar. 9	223	95	Richards	Recrystallized Baker 10%	Second half. 7200.94	0.509426	4097.79	1.11707	
	224	93	Poggendorff	Frankfurt 10%			98.10	715	With silk
	225	127	Richards	Recrystallized Baker 10%			97.92	710	
	226	128	Poggendorff	Frankfurt 10%			98.28	720	Do.
	227	27	Rayleigh	do			98.27	720	Filter tube from PTR
	...	126	Richards	do			....	....	Spoiled; accident in washing.
	228	125	Rayleigh	do			99.02	740	BS filter tube, not washed
	...	28	Richards	do			....	....	Spoiled; deposit grew through porous cup
12	229	95	do	do	7201.40	0.509432	4098.83	1.11727	Cup water washed. Trace of alkali
	230	127	do	do			98.92	729	Do.
	231	27	do	do			98.38	714	Cup water washed
	232	28	do	do			98.87	728	Cup acid washed. Baked 700°
	233	125	do	do			98.26	711	Cup water washed
	234	126	do	do			98.19	709	Cup water washed. Baked 700°
16	235	127	Poggendorff	do	7201.82	0.509424	4098.28	1.11707	With silk
	236	128	do	Baker 10%			98.62	716	Do.
	237	27	Richards	Frankfurt 10%			98.69	718	At 50° C. Trace of alkali
	238	28	do	do			98.09	702	At room temperature
	239	125	do	Recrystallized Baker 10%			98.09	702	At 50° C.
	240	126	do	do			98.09	702	At room temperature

19	241	95	do	Frankfurt 10%	7201.17	0.509427	4097.96	1.11709	New cup, water washed. Trace alkaline
	242	93	do	do			97.94	709	Old cup, water washed. Trace alkaline
	243	127	do	do			97.63	700	New cup, water washed. Trace alkaline.
	244	128	do	do			97.65	701	Old cup, water washed. Trace alkaline
	245	27	do	do			97.22	689	Old cup, water washed. Baked, alkaline
	246	28	do	do			97.62	700	New cup, water washed. Trace alkaline
	247	125	do	do			97.27	690	Old cup, water washed. Trace alkaline
	248	126	do	do			97.38	693	New cup, acid washed. Baked, alkaline
23	249	95	do	do	7202.15	0.509422	4099.05	1.11723	
	250	93	do	Recrystallized Baker 10%			98.42	706	
	251	127	do	Frankfurt 10%			98.88	718	
	252	128	do	Recrystallized Baker 10%			98.32	703	
	253	27	do	Frankfurt 10%			98.69	713	At room temperature
	254	28	do	do			98.57	710	At 50° C
	255	125	do	Recrystallized Baker 10%			98.24	701	At room temperature
	256	126	do	do			98.11	698	At 50° C
26	257	95	do	Recrystallized Frankfurt 10%	2 hours	½ amp.	4098.84	....	
	258	93	do	Recrystallized Baker 10%			98.96	....	
	259	127	do	Recrystallized Frankfurt 10%			98.89	....	
	260	128	do	Recrystallized Baker 10%			98.98	....	
	261	27	do	Recrystallized Frankfurt 10%			98.62	....	
	262	28	do	Recrystallized Baker. 10%			98.78	....	
	263	125	Rayleigh	do			99.65	....	PTR filter tube
	264	126	do	do			99.66	....	BS filter tube washed

TABLE 1—Continued

General Table of Quantitative Results for 1910—Continued

Date	No.	Bowl	Form	Electrolyte	Time	Current	Deposit	Electrochemical equivalent	Remarks
					sec.	amp.	mg.		
Mar. 31	265	95	Richards	Recrystallized Frankfurt 10%	Second half. 7202.78	0.509414	4098.63	1.11704	
	266	93	do	Electrolyzed Frankfurt 10%			99.19	719	Spot in bowl on silver
	267	26	do	Baker 10%			98.91	711	
	268	127	do	Electrolyzed Baker 10%			98.79	708	
	269	128	do	do			98.77	708	
	270	27	do	Electrolyzed Frankfurt 10%			98.51	701	
	271	28	do	Frankfurt 10%			98.71	706	
	272	125	do	Recrystallized Frankfurt 10%			98.42	698	
	273	126	do	Frankfurt 10%			98.70	706	
Apr. 5	274	27	do	Electrolyzed Frankfurt 10%	7198.98	0.509474	4099.61	1.11778	Experiment abnormal, due to probable contamination of electrolyte, deposits striated.
	275	28	do	Recrystallized Frankfurt 10%			4100.05	788	
	276	125	do	Frankfurt 10%			4099.96	785	
	277	126	do	Filtered Baker 10%			4098.10	725	

C. CLASSIFIED RESULTS

1. THE SMALL POROUS CUP VOLTAMETER

During this period of the work we found the small porous cup voltameter to be the most reliable and convenient form to use as a standard. It possesses important advantages in ease of manipulation, economy of materials, and reliability of results. Table 2 shows the results of 44 deposits made, using the four small voltameters. Two of these were gold and two platinum cups, all being of the same weight and capacity. The electrolyte was in most cases new, prepared from pure silver nitrate as purchased, without recrystallization. In all but four cases it was 10 per cent electrolyte, in two cases it was used solution brought up to 10 per cent by adding new salt, in a few cases it differed in other particulars, all of which are noted in the table.

The average value is 1.11703 mg per coulomb, as defined in Part I, page 190. This corresponds to a value of 1.01827_5 volts for the Weston Normal Cell at 20° C. The average variation of a single determination from the mean is 3 parts in 100 000, which we consider a satisfactory result, considering that variations in the measurement of time and current enter as well as appreciable variations in the electrolyte.

The deposits were uniform in character, white in color, always nonstriated, adherent, and crystalline as seen under the microscope. There is very little loose silver, and by the method of washing employed this is left in the cups, so that it is seldom necessary to return silver in appreciable quantity to the cups. We believed the silver nitrate to be very pure, but had at this time no sure criterion as to how near it was to absolute purity. Subsequent work with electrolytes conforming to the tests described in Section II of this paper has confirmed our belief in the accuracy of the results obtained, using the small porous cup voltameter.

TABLE 2

Summary of Results using Small Richards Voltameters, Second Series

Date	No.	Electro-chemical equivalent	Electrolyte	Remarks
1909				
Dec. 17	128	1.11698	15% Frankfurt AgNO$_3$	Coarse porous cup
	129	707	.....do	
	130	700	.....do	
	131	708	.....do	
1910				
Jan. 26	158	704	10% Frankfurt AgNO$_3$	
	159	709	.....do	
28	161	702	.....do	
	162	700	.....do	Filtered through bulb
	163	701	.....do	
	164	701	.....do	Do.
Feb. 8	175	704	.....do	
	177	700	.....do	
10	179	707	.....do	
	181	700	.....do	
15	187	704	.....do	
	188	704	.....do	Used + added salt
	189	702	.....do	Do.
	190	696	.....do	
19	195	702	.....do	Filtered through asbestos
	196	704	.....do	
	197	701	.....do	
	198	702	.....do	Do.
23	200	702	.....do	
	201	697	.....do	
25	203	704	.....do	
	204	701	.....do	A little acid present
	205	699	.....do	Do.
	206	696	.....do	
Mar. 2	213	707	.....do	
	214	711	.....do	
5	{ 220 221 }	708	.....do	2 in parallel, 4 hours
	222	706	.....do	
12	231	714	.....do	
	233	711	.....do	
16	238	702	.....do	
	240	702	.....do	Recrystallized AgNO$_3$
19	246	700	.....do	
	247	690	.....do	
23	253	713	.....do	
	255	701	10% Baker AgNO$_3$	Recrystallized
31	270	701	10% Frankfurt AgNO$_3$	Electrolyzed
	271	706	.....do	
	272	698	.....do	2 recrystallizations
	273	706	.....do	

Mean of 44 = 1.11703; mean variation = ±3.
Value for Weston Normal Cell = 1.01827$_5$ at 20° C on present basis.[4]

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[4] Circular of the Bureau of Standards, No. 29.

In order to show the reproducibility of the small porous cup voltameter, the weights of 54 deposits made in pairs (except two sets of three each), in which the electrolyte and other conditions were as nearly identical as possible in the two cups of each pair, have been tabulated. The following paragraph, written two years ago, still represents our views concerning the possibilities of this type of voltameter:

> The average deviation of each value from the mean of each group of two or three is only *one part in one hundred thousand*. That is, when the variations in the measurement of current and time are eliminated and the variation in the electrolyte is removed, so that it is simply a question of how nearly two similar voltameters agree with one another, and the variation is that produced by the loss of silver, fluctuation in moisture or impurity in the deposit, and the error of weighing the cups before and after the deposit, the average deviation of a cup from the mean of a pair is only one-thousandth of 1 per cent, the deposit being 4 grams and the number of deposits 54, extending through a period of three months. If the single deposits agree so closely and the average deviation from the mean of 44 deposits is only 3 parts in 100 000, it is evident that the small porous cup voltameter, as we have used it, is an instrument of high precision and capable of serving as a means of checking the constancy of the Weston Normal Cell, as the London Conference has declared it must be employed to do, *provided* there is no uncertainty in its use which we have not discovered, and that it is possible to obtain silver nitrate of so uniform purity that no appreciable variation in value will occur in future use due to changes in the degree of purity of salt employed.

TABLE 3

Showing the Reproducibility of the Small Porous Cup Voltameter

[The deposits made under the same conditions are arranged in groups. In column Δ are tabulated the differences of each member of the group from the group mean. The average of these differences for 54 deposits is 0.04 mg or 1 part in 100 000 of the deposit.]

Date	No.	Deposit	Mean	Δ
1909		mg.	mg.	mg.
Dec. 17	128	4096.93	4097.00	0.07
	130	6.98		.02
	131	7.10		.10
1910				
Jan. 7	138	8.04	8.04	.00
	140	8.10		.06
	141	7.97		.07
13	145	6.34	6.34	.00
	146	6.34		.00

TABLE 3—Continued

Showing the Reproducibility of the Small Porous Cup Voltameter—Contd.

Date	No.	Deposit	Mean	Δ
1910		mg.	mg.	mg.
Jan. 26	158	4097.41	7.48	.07
	159	7.56		.08
	157	6.78	6.84	.06
	160	6.91		.07
28	161	6.97	6.95	.02
	163	6.94		.01
	162	6.89	6.91	.02
	164	6.93		.02
31	165	3.51	3.53	.02
	166	3.55		.02
Feb. 3	167	0.93	0.94	.01
	170	0.95		.01
	168	0.89	0.86	.03
	169	0.84		.02
8	175	7.39	7.38	.01
	177	7.38		.00
	176	7.09	7.06	.03
	178	7.03		.03
10	179	8.69	8.72	.03
	181	8.74		.02
	180	8.30	8.26	.04
	182	8.23		.03
12	185	5.04	5.05	.01
	186	5.05		.00
15	187	7.42	7.25	.16
	190	7.10		.16
	188	7.43	7.38	.05
	189	7.34		.04
17	191	7.84	7.77	.07
	194	7.69		.08
	192	7.63	7.61	.02
	193	7.59		.02

TABLE 3—Continued

Showing the Reproducibility of the Small Porous Cup Voltameter—Contd.

Date	No.	Deposit	Mean	Δ
1910		mg.	mg.	mg.
Feb. 19	195	4098.68	8.68	.00
	198	8.69		.01
	196	8.77	8.70	.07
	197	8.64		.06
23	200	8.79	8.70	.09
	201	8.62		.08
25	203	8.46	8.30	.16
	206	8.15		.15
	204	8.33	8.30	.03
	205	8.28		.02
Mar. 12	231	8.38	8.32	.06
	233	8.26		.06
31	271	8.71	8.70	.01
	273	8.70		.00
			Average...	.04

2. THE LARGE POROUS CUP VOLTAMETER

Table 4 gives the results of 28 deposits in the large and medium cups, using 10 per cent Frankfurt electrolyte mostly, but with a few deposits from Baker, new or recrystallized, or electrolyzed, and a few from Frankfurt used and recrystallized. The mean value for all is 1.11710, or omitting two deposits, Nos. 229 and 230, 1.11709, with an average variation from the mean of 4 parts in 100 000, not quite as uniform agreement as with the small cups, but it will be noticed that there are a good many varying conditions.

TABLE 4

Deposits in Large and Medium Size Richards Voltameters

Date	No.	Size	Electro-chemical equivalent	Porous cup	Electrolyte
1909					
Dec. 17	122	l.	1.11705	Large porous cup........	15% Frankfurt $AgNO_3$
	124	l.	711	.....do..................	10% Frankfurt $AgNO_3$
	125	m.	701	.....do..................	Do.
1910					
Jan. 7	135	m.	706	.....do..................	10% Baker
13	144	l.	709	.....do..................	10% Frankfurt
21	149	l.	714	Small porous cup........	7.5% used Frankfurt
	150	m.	712	Large porous cup........	10% new Frankfurt
Mar. 9	223	l.	707	Small porous cup........	10% Baker, twice recrystallized
	225	m.	710	.....do..................	Do.
12	229	l.	727	Small, trace of alkali....	10% Frankfurt
	230	m.	729		
19	241	l.	709	Small new cup..........	Do.
	242	l.	709	Small old cup...........	Do.
	243	m.	700	Small new cup..........	Do.
	244	m.	701	Small old cup...........	Do.
23	249	l.	723	Small porous cup	Do.
	250	l.	706	.....do..................	10% Baker recrystallized
	251	m.	718	.....do..................	Frankfurt
	252	m.	703	.....do..................	Baker recrystallized
26	257	l.	706	.....do..................	10% Frankfurt recrystallized
	258	l.	709	.....do..................	10% Baker recrystallized
	259	m.	708	.....do..................	10% Frankfurt recrystallized
	260	m.	710	.....do..................	10% Baker recrystallized
31	265	l.	704	....	10% Frankfurt recrystallized
	266	l.	719	....	10% Frankfurt electrolyzed
	267	m.	711	....	10% Baker
	268	m.	708	....	10% Baker electrolyzed
	269	m.	708	....	Do.

Mean of 28 deposits = 1.11710
Mean of 26 deposits = 1.11709, omitting (229 and 230) $\pm 4/10^6$
Mean of 18 deposits = 1.11708, omitting 8 relative deposits

The value 1.11709 corresponds to 1.01833 volts for the Weston Normal Cell at 20° C, assuming the electrochemical equivalent of silver to be 1.11800 mg per coulomb, as explained on page 190. This is 6 in 100 000 larger than the mean of 44 deposits in small cups. We regard this difference of 6 in 100 000 as of particular significance and discuss it at length on page 514.

3. POGGENDORFF VOLTAMETER

Table 5 gives the results of 17 deposits in the Poggendorff voltameter, the first 7 having been made without silk or any septum, and the last 10 with pure raw silk that had been thoroughly washed with hot distilled water. In the first 3 the deposits were much too heavy, but the next 4 were about normal for the kinds of electrolyte used. In the later deposits, using washed silk, the deposits average 1.11712, or omitting No. 219 of a four-hour run, which gave a high value and No. 236 made with less pure salt, the average is 1.11710. This is nearly in agreement with the porous cup voltameter, which for this size of voltameter ought to average about 1.11706. The difference is too small to be sure of, unless more deposits are made under identical conditions.

TABLE 5

Summary of Deposits in the Poggendorff Voltameters

Date	No.	Size	Electro-chemical equivalent	Septum	Electrolyte
1909					
Dec. 17	123	l.	1.11849	No silk............	15% Frankfurt salt
	126	m.	733	.....do............	Do.
	127	m.	738	.....do............	Do.
1910					
Jan. 7	136	m.	710	.....do............	10% Baker
	137	m.	709	.....do............	Do.
21	151	m.	708	.....do............	Used electrolyte filtered through porous cup
	152	m.	707	.....do............	New electrolyte filtered through porous cup
Feb. 25	207	m.	701	Washed silk......	10% Frankfurt
	208	m.	707	.....do............	Do.
Mar. 2	215	m.	707	.....do............	Do.
	216	m.	713	.....do............	Do.
5	218	m.	712	.....do............	Do.
	219	m.	721	.....do............	Do.
9	224	m.	715	.....do............	Do.
	226	m.	720	.....do............	Do.
16	235	m.	707	.....do............	Do.
	236	m.	716	.....do............	10% Baker

Mean of last 10=1.11712
Mean of last 10=1.11710 (excluding 219 and 236)

The mean is very nearly the same as that found with large and medium porous cup voltameters, being 1.11710 as compared with 1.11709. The value of 1.11710 mg per coulomb corresponds to 1.01834 volts for the Weston Normal Cell at 20° C, assuming the electrochemical equivalent of silver to be 1.11800 mg per coulomb as fixed by the London Conference of 1908.

4. SIPHON VOLTAMETER

The siphon form of voltameter has been employed by some observers as a test for the reliability of other forms. We therefore made some study of its performance under varying conditions. We have made 11 deposits altogether in the siphon form of voltameter, using both large and small cups and large and small glass siphons (see our first paper, p. 174). The runs are relative, but have always been compared with the Richards form of voltameter, and from the assumed values of the latter the electrochemical equivalent of the siphon form is found.

TABLE 6

Results with the Siphon Voltameters

Date	No.	Electrolyte	Electrochemical equivalent	Remarks
1910				
Jan. 7	133	Baker 10%..............................	1.11740	Large bowl
	134	.....do....................................	740	Do.
13	142	Frankfurt 10%..........................	726	Do.
	143	.....do....................................	727	Do.
21	147	Used Frankfurt.........................	720	Do.
	148	.....do....................................	707	Porous cup over cathode end
Feb. 12	183	Frankfurt 10%..........................	720	Porous cup over anode end
	134	.....do....................................	717	Large bowl
Mar. 2	209	.....do....................................	756	2 large bowls in parallel
	210	.....do....................................		
	211	.....do....................................	743	2 small bowls in parallel
	212	.....do....................................		
5	217	.....do....................................	774	2 siphons in 1 large bowl

Mean, 1.11736.
The corresponding value for the Weston Normal Cell at 20° is 1.01858.

The first two deposits (Nos. 133 and 134), using Baker $AgNO_3$, agree with one another, giving 1.11740. The next two, January 13, with Frankfurt $AgNO_3$, somewhat purer, give lower values, 1.11726 and 1.11727. In the third trial, January 21, with a used solution we obtained 1.11720 and 1.11707, but in the latter *a porous cup was placed over the cathode end of the siphon and was therefore equivalent to a Richards voltameter.* In the fourth trial, February 12, the values were nearly alike, 1.11720 and 1.11717, the first having a porous cup over the anode end. It was therefore equivalent to a Richards voltameter of very large volume. In the fifth trial, March 2, there were two large siphon voltameters in parallel, equivalent to one of double volume, and the current was one-fourth ampere in each for four hours. The value is very high, 1.11756. There were also two smaller siphons in parallel, using small cups. They gave 1.11743, still a large value. In the sixth trial we employed two large siphons dipping into one large platinum dish, with two anodes in parallel. An 8-gram deposit was made, giving 1.11774, the largest of all. We thus have 10 deposits (excluding No. 148, which was a Richards of usual volume), which gives a mean value of 1.11736, about 30 parts in 100 000 greater than the small-size Richards voltameter. The values vary greatly with the volume of the electrolyte. We thought it possible that if the $AgNO_3$ were perfectly pure the different sizes would give the same values and that they would be correct. We have later found this to be true. But the variation of the results in our experience is so large and they are so awkward to use that we have seldom used them since.

5. FILTER PAPER VOLTAMETER

We made very few experiments with this form of voltameter, owing to the errors shown to exist in it by the results of the first series of experiments. The few determinations recorded here were for the purpose of trying out special features.

Table 7 gives the results of seven deposits, using filter paper. The first deposit (No. 132) was made with a smaller quantity of the filter paper immersed in the electrolyte than usual, more nearly as Mr. Smith has done in his work. The deposit nearly agrees with his value. Nos. 199 and 202 corresponded to the earlier arrangement and give about the same values as we then obtained. The next two deposits give a comparison of two filter tubes, one of which was received from the Reichsanstalt and the other was from our own stock, but like the first, except that it had not been washed previous to use. The latter gave a much heavier deposit. Accordingly, we made two other deposits (Nos. 263 and 264), in which we washed our filter tube thoroughly and treated it with dilute alkali, and then washed again with distilled water. The alkali dissolves out in considerable degree the furfural-yielding carbohydrates. The deposits with the Reichsanstalt tube and our own then agreed exactly, but both are considerably heavier than with porous cup voltameter.

Chemical tests show that while this special treatment of filter paper makes it less readily decomposed into furfuraldehyde, the filter paper thus treated never becomes entirely resistant, and hence the deposit will always be abnormally large.

TABLE 7

Summary of seven deposits in Filter Paper Voltameter

Date	No.	Electro-chemical equivalent	Filter paper	Electrolyte
1910				
Jan. 7	132	1.11723	Small quantity of filter paper................	10 % Baker salt
Feb. 23	199	746	1 sheet filter paper..........................	10 % Frankfurt
	202	751	.....do.......................................	Do.
Mar. 9	227	720	Small filter tube from PTR................	Do.
	228	740	Small filter tube from BS..................	Do.
26	263	726	Small filter tube from PTR................	10 % Baker recrystallized
	264	726	Small filter tube from BS washed..........	Do.

Mean of 7=1.11733.

The corresponding value for the Weston Normal Cell at 20° is therefore 1.01855 volts.

D. SPECIAL QUESTIONS

1. USED SOLUTIONS

In connection with the first series of experiments, some discussion has been given of the effects observed when an electrolyte is used in the voltameter for the second or third time. The fact has been noted that used solutions free from filter paper or other contamination give normal or slightly smaller deposits than the same solution unused. In the case of electrolytes containing traces of impurities, such as those made from the salt as generally purchased, the lower deposit may be due in part at least to the purifying effect of previous electrolysis.

As a rigid test of this, we have successively electrolyzed a solution of silver nitrate which was strongly contaminated with filter paper until it gave a deposit of well-formed crystals free from striations. The electrolyte was 15 per cent $AgNO_3$, which had stood in contact with filter paper for several months. It was electrolyzed in a small voltameter at normal current density, but without septum between the anode and cathode in order to maintain the concentration of the electrolyte. As might be expected, the first deposit was strongly striated and leaden colored. This deposit was removed and the electrolysis begun again. The second, third, and fourth deposits were all strongly striated and not crystalline. The fifth deposit was also striated, but a few crystal faces were to be seen. These increased in number in the succeeding sixth, seventh, eighth, and ninth deposits, and at the same time the striations were becoming less and less prominent. In the tenth deposit the striations completely disappeared and the crystalline structure was good. This matter seemed so important that we made several similar experiments to confirm it. In these we successively electrolyzed solutions contaminated with filter paper and others with meta-furfuraldehyde. The result was the same in all cases. We found the impurities could be eliminated by sufficiently prolonged electrolysis. We shall refer to this phenomenon again in discussing the "volume effect" on page 514.

During the present series of quantitative experiments we have employed used solutions in the runs of January 21, February 5, 8, 15, 17, March 31, and April 5. The experiments of February 8, 15, and March 31 were made expressly to test the effect of previous electrolysis. In the others, except the abnormal experiment of April 5, we introduced other variations. In the first of these three we used a clear anode solution saved from the Richards voltameter of previous experiments. Two deposits were made from this electrolyte in the small voltameters and compared with two similar deposits from our 10 per cent Frankfurt salt. The results are as follows:

Anode liquid		Frankfurt electrolyte	
No. 176	1.11695	No. 175	1.11704
No. 178	1.11694	No. 177	1.11703

Deposit from anode liquid is less by 8 parts in 100 000.

In the experiment of February 15 we compared the cathode liquid (from the Richards voltameter) to which we added enough Frankfurt crystallized salt to bring the concentration up to 10 per cent with a 10 per cent new solution of the Frankfurt electrolyte and found the two in good agreement.

Used+added salt		Frankfurt electrolyte	
No. 188	1.11704	No. 187	1.11704
No. 189	1.11702	No. 190	1.11696

No. 190 probably abnormally low, owing to accident.

It thus appears that used solutions yield normal results if some fresh salt is added to keep up the concentration of the electrolyte.

On March 31 we compared our Baker and Frankfurt salt with recrystallized and electrolyzed samples. Except for No. 266, which was abnormally heavy owing to a spot found on the silver deposit when the bowl was weighed, the results show that the values for the electrochemical equivalent from the recrystallized and elctrolyzed samples are lower than from the original salt.

TABLE 8

No.	Size	Original salt		Electrolyzed		Recrystallized Frankfurt
		Baker	Frankfurt	Baker	Frankfurt	
265	l.	....	....	....	....	1.11704
266	l.	....	....	....	(1.11719)	....
267	m.	1.11711	....	....	....	....
268	m.	....	....	1.11708	....	....
269	m.	....	....	1.11708	....	....
270	s.	....	....	....	1.11701	....
271	s.	....	1.11706	....	....	....
272	s.	....	....	....	....	1.11698
273	s.	....	1.11706	....	....	....
Means..........		1.11711	1.11706	1.11708	1.11701	1.11701

The significance of these figures will be brought out in the next section.

2. VOLUME EFFECT

By comparing the results of the two sizes of porous cup voltameters (Tables 2 and 4) it will readily be seen that the deposits in the large size are with few exceptions heavier than in the small voltameters. The difference amounts to about 7 parts in 100 000. This phenomena we have called the *volume effect*. In these experiments the volume of electrolyte in the large voltameters was about three times that in the small voltameters. We find evidence of this volume effect in the work of Lord Rayleigh and Mrs.

Sedgwick.[5] Employing voltameters with a greater disparity in volume the effect is made still more apparent. This is shown in our results with the siphon voltameter and is in accord with the observations of Laporte and de la Gorce.[6]

Since we regard this matter of the volume effect as of considerable importance we shall state rather fully the evidence for believing in its reality and our theory as to its probable cause and the means of avoiding it.

During the earlier part of the work when using the largest size of porous pots in the large-size platinum bowls the volume of the cathode liquid was but little greater than that in the small voltameters. The resulting disparity in the deposits being therefore small was usually attributed to experimental error. But when using the small-size porous cups in the large voltameters, with a larger volume of the cathode liquid, the difference became more apparent. On making an examination of the records it appeared that the large voltameters in practically every case contained heavier deposits than the smaller sizes. By taking the two voltameters in pairs, identical in all respects except the volume of the electrolyte, we were forced to conclude that the observed difference is a function of the volume.

Judging the electrolyte used in these runs by present standards of purity, we find them to have been far from absolutely pure. This suggests the probable cause for the volume effect and is supported by the following evidence. In the curves shown in figures 1 and 2 the slope of the lines is a measure of the volume effect. The steeper curve represents the volume effect of the electrolyte as purchased, while the more nearly horizontal line represents the volume effect of the same salt after purification by electrolysis in the voltameter or by recrystallization. With an electrolyte of sufficient purity all sizes of voltameters should give the same weight of deposit, provided the volume is the only variable. In our latest work we have attained such a degree of purity of the electrolyte that the volume effect vanishes.

As before stated, we place greater reliance on determinations with the small porous cup voltameter with solutions not quite pure than on any other form. The reason for this is that with so small a volume the effect of the impurities is very much less than for the greater volumes. This is shown by the wide divergence of the above curves of figures 1 and 2 for volumes of 200 cc or over.

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[5] Phil. Trans., 175, p. 411; 1884.

[6] Bull. Soc. Int. Electr., March, 1910.

In the case of the porous cup voltameter the volume of electrolyte considered is that of the cathode chamber only and not the total volume of liquid in the voltameter; this conclusion is justified by the following observations:

TABLE 9

Date	No.	Form	Total volume of electrolyte	Volume of cathode liquid	Deposit
1910			cc		mg
Jan. 21	147	Siphon	500	....	4149.11
	148	Siphon, porous cup over cathode end	500	210	4148.58
	149	Richards	340	320	4148.86
	153	.....do	115	90	4148.47
Feb. 12	184	Siphon	500	....	4105.63
	183	Siphon, porous cup over anode end	500	450	4105.75
	185	Richards	115	90	4105.04
	186	.....do	115	90	4105.05

These results show that when the porous cup is over the anode end of the siphon the weight of deposit is substantially the same as for the siphon voltameter without any septum, while for the case of the pot over the cathode end the volume of liquid contained inside of it and the siphon is without effect.

The cause of this effect we believe to be the presence of reducing impurities and consequent colloidal silver in the electrolyte. Solutions showing the volume effect can be shown to be impure by a test with potassium permanganate as described on page 531. Since the colloidal silver can not pass through the porous pot, it is only the volume of the cathode liquid that should be effective in increasing the deposit, which is in accord with experimental data. Impurities which are not sufficient to cause striations may be sufficient to produce a small volume effect, and *therefore we may use this as a more rigid criterion by which to judge the purity of the electrolyte than the appearance of the deposit.*

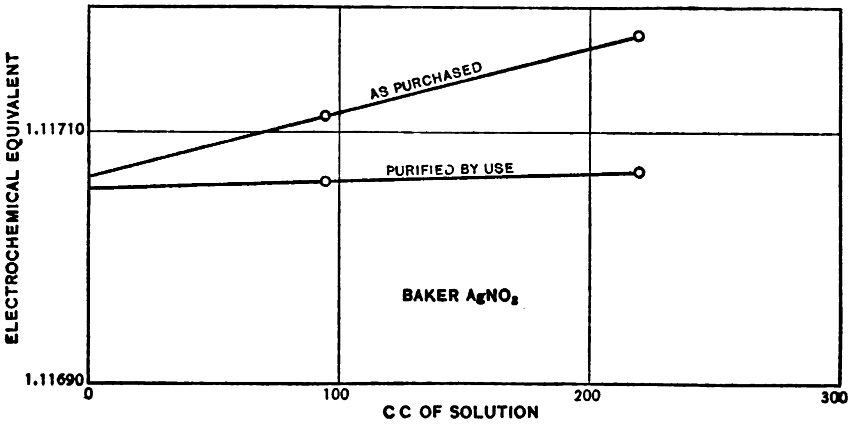

Fig. 1.

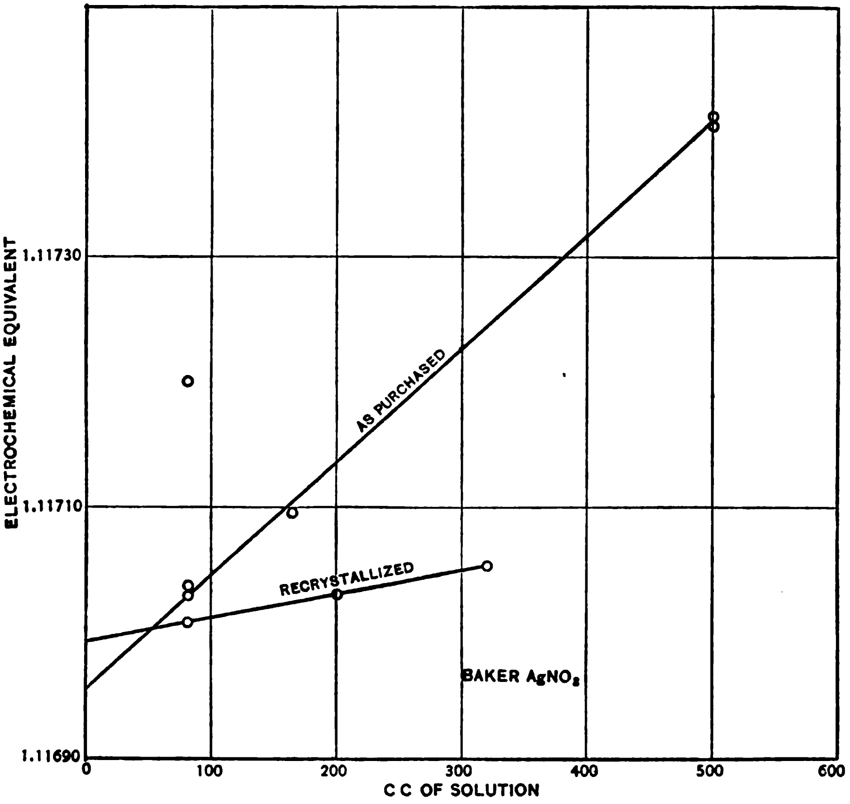

Fig. 2.

Figs. 1 and 2.—*Effect of purification of the* $AgNO_3$ *on the volume effect which is represented by the slope of the curves.*

With a relatively small volume of electrolyte the quantity of colloidal silver deposited during a given time is less than with a larger volume. Gradually the colloidal silver is deposited out and the electrolyte becomes purer, and hence a used solution may give a more nearly normal value than a new solution. Hence, with solutions not quite pure we see why the smaller voltameters give more consistent and more nearly correct values than larger voltameters.

3. ANODE SLIME IN THE POGGENDORFF FORM

The cause of the wide variations in the results of the Poggendorff or nonseptum form of voltameter we attributed to the difficulty of confining the anode slime. The results tabulated in Table 5 show an average variation from the mean of 9 parts in 100 000, which is an unfavorable showing as compared with our results on the porous cup voltameter. The first seven of the deposits in the table show a larger mean variation than the average given above, and this is almost entirely due to anode slime becoming mixed with the deposited silver. Small bubbles of gas liberated by the warming of the electrolyte or from other causes carry small masses of slime to the surface of the liquid. When the gas is discharged the slime falls back, sometimes upon the cathode. We have investigated various means of separating it from the crystalline deposit, but have found no process that is satisfactory. The best perhaps is by stirring the liquid when the finely divided slime is carried in suspension for a short time by the liquid, leaving the larger particles of crystalline silver in the bottom of the dish. Some have effected the separation by means of a glass rod or feather, but we believe that this calls unduly upon the judgment of the observer, and we fail to find in such cases as small a variation from the mean as we believe may reasonably be expected. To avoid the trouble with slime we covered the anode with silk, but this is not satisfactory, because the silk is an active agent in the voltameter playing a somewhat similar rôle to filter paper.

Our results have confirmed those of Mr. F. E. Smith, who found that the trouble with slime from the anode may be greatly reduced by using electrolytic anodes with as large an active surface as possible. Such anodes possess the advantage of providing silver of a high degree of purity and of an even hardness. The advantages of the former are apparent, while the latter tends to reduce the slime. We have observed with anodes of pure silver that have been rolled or sawed that a disintegration takes place under the surface, causing considerable pieces of it to fall off, accompanied by much black slime. This appears to depend upon the surface hardness of the metal. With anodes sufficiently covered with pure electrolytic silver the wearing away of the surface is uniform, and only a small quantity of gray slime appears.

4. FILTERING THE ELECTROLYTE

In May, 1909, we arranged to use a porous cup as a filter, employing the vacuum to hasten the process. It was first used in the experiment of May 6 and occasionally thereafter. We were not able to detect any change in the mass of deposit due to its use. The question was again taken up in the work of 1910, during which time we tried two Pasteur filters, designated as No. 1 and No. 2, and a little bulb of Pukal ware.

These were carefully cleaned before use. The results are given in Table 10. In making these tests we always used four small porous cup voltameters, two of which contained the filtered solution and two the same electrolyte not filtered.

Filter No. 1, which was used first, showed a surprising reduction of 15 parts in 100 000 in the deposit. We repeated this experiment, using the Pukal bulb, which caused no change in the deposit. Using filter No. 1 in a subsequent experiment we again found a reduction in the deposit amounting to 13 parts in 100 000. We then filtered one portion of electrolyte through filter No. 1 and another portion through an identically similar filter No. 2, which had not been acid cleaned. The deposit from the first gave a deposit 5 in 100 000 lower than the other, but this difference may have been due to a trace of alkalinity persisting in filter No 2, since it was not cleaned with acid. While it appeared that the Pukal bulb, like the porous pot previously used, was reliable as a filter, the contradictory evidence of the Pasteur filters led us to try purified asbestos as a filter with satisfactory results. The asbestos can be quickly prepared and expeditiously used. In our subsequent work we preferred to use it when it was necessary to use a filter of any kind. In using either the asbestos or the Pukal filter it is best to discard the first portion of filtrate, owing to the tendency for acid to form before equilibrium is established between the solution and the filter.

TABLE 10

Showing the Effect of Filters on the Electrolyte

Date	No.	Electro-chemical equivalent	Remarks
1910			
Jan. 26	157	1.11687	Electrolyte filtered through filter No. 1
	160	691	Do.
	158	704	Electrolyte not filtered
	159	709	Do.
28	162	700	Electrolyte filtered through bulb
	164	701	Do.
	161	702	Electrolyte not filtered
	163	701	Do.
Feb. 10	180	696	Electrolyte filtered through filter No. 1
	182	694	Do.
	179	707	Electrolyte not filtered
	181	708	Do.
17	192	696	Electrolyte filtered through filter No. 1
	193	695	Do.
	191	702	Electrolyte filtered through filter No. 2
	194	698	Do.
19	195	702	Electrolyte filtered through asbestos
	198	702	Do.
	196	704	Electrolyte not filtered
	197	701	Do.

5. TEMPERATURE COEFFICIENT OF THE VOLTAMETER

Two tests of the effect of temperature on the mass of deposit were made, using in each case the four small voltameters, two of which were maintained at about 50° during the course of the experiment by heating coils wound on asbestos forms and made to fit closely about the platinum crucible. The temperature of each was obtained from thermometers standing in the porous cup of each voltameter. The temperatures were read every 10 minutes. The following curve shows them plotted against time for the second experiment (fig. 3):

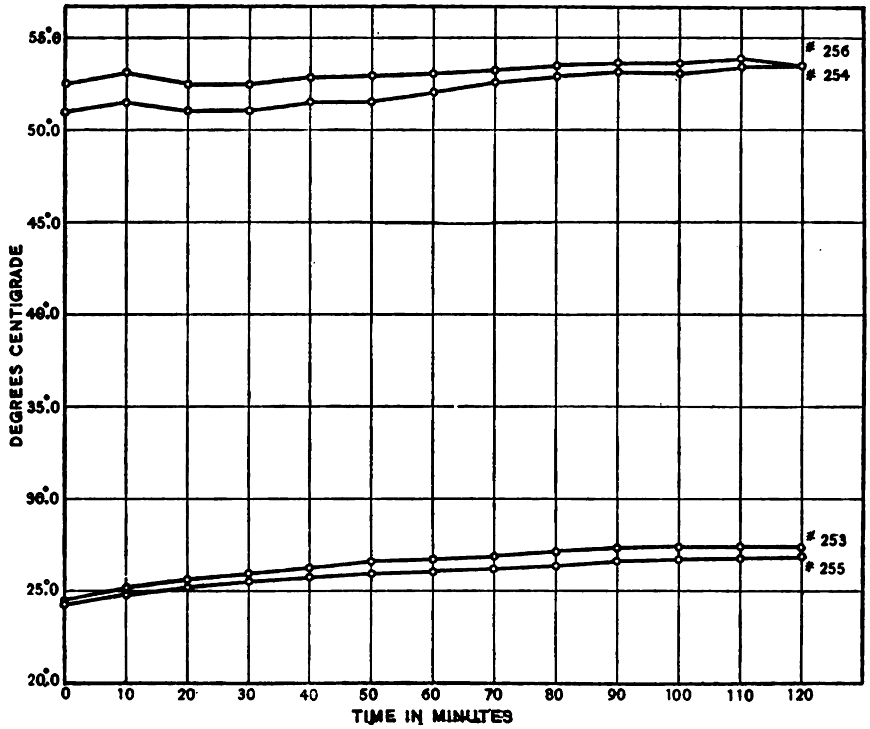

Fig. 3.—*Record of temperatures of four voltameters during the second experiment to determine the temperature coefficient.*

The results are contained in Table 11.

TABLE 11

Experiments on Temperature Coefficient

[The deposits in Nos. 256 and 255 are lower than Nos. 254 and 253 because the electrolyte was made from purer salt]

Date	No.	Electro-chemical equivalent	Remarks
1910			
Mar. 16	237	1.11718	Heated to 51° C (average)
	239	702	Heated to 55° C (average)
	238	702	Not heated, 23° C (average)
	240	702	Do.
23	254	710	Heated to 52° C (average)
	256	698	Heated to 53° C (average)
	253	713	Not heated, 26° C (average)
	255	701	Do.

In the first run the heated voltameters showed an average of 9 parts in 100 000 greater deposit, the difference of temperature being 29.5°, while the second experiment showed 3 parts in 100000 smaller deposit in the heated voltameters, the difference in temperature being 26.5°.

The differences are probably due to experimental error, particularly in the case of No. 237, in which a trace of alkali was found after the experiment. The temperature coefficient deduced from these experiments is not more than one or possibly two parts in a million per degree and is more likely zero for perfectly pure solutions as it should be theoretically.

6. COMPARISON OF GOLD AND PLATINUM CATHODES

In the summer of 1909 we purchased two gold crucibles of the same dimensions and weight as the two platinum dishes, which we had found very useful. These four were usually arranged in pairs of one gold dish and platinum dish, each so that by tabulating the differences in deposit of the two crucibles of a pair we have a direct comparison of gold and platinum cathodes. This has been done in Table 12 for all cases where the material of the cathode was the only variation in the voltameter except for obviously abnormal determinations on January 7 and 21.

The result is to show a lighter deposit in the gold dishes by 1.4 parts in 100 000. This difference is less than the average variation from the mean of our most reliable determinations of the electrochemical equivalent and we regard it, therefore, as indicating the substantial agreement of the two materials.

TABLE 12

Comparison of Gold and Platinum Cathodes

Date	Gold dish	Platinum dish	Difference (parts in 10^5)
1909			
Sept. 9	4097.99	4098.21	−5.4
Dec. 17	4096.98	4096.93	+1.2
	4097.10	4097.27	−4.1
1910			
Jan. 7	4098.10	4098.04	0.0
	4097.97	....	....

TABLE 12—Continued

Comparison of Gold and Platinum Cathodes—Continued

Date	Gold dish	Platinum dish	Difference (parts in 10^5)
1910			
Jan. 26	4096.91	4096.78	+3.2
	4097.56	4097.41	+3.7
28	4096.94	4096.97	−0.7
	4096.93	4096.89	+1.0
31	4163.55	4163.51	+1.0
Feb. 3	4130.84	4130.89	−1.2
	4130.95	4130.93	+0.5
8	4097.38	4097.39	−0.2
	4097.03	4097.09	−1.7
10	4098.74	4098.69	+1.2
	4098.23	4098.30	−1.7
15	4097.34	4097.43	−2.2
	4097.10	4097.42	−7.8
17	4097.69	4097.84	−3.7
	4097.59	4097.63	−1.0
19	4098.64	4098.77	−4.1
	4098.69	4098.68	+0.2
23	4100.59	4100.41	+4.4
	4098.62	4098.79	−4.1
25	4098.28	4098.33	−1.2
	4098.15	4098.46	−7.8
Mar. 2	4097.25	4097.62	−9.3
16	4098.09	4098.09	0.0
	4098.09		
31	4098.70	4098.71	−0.2
	4098.42	4098.51	−2.2
		Average	−1.4

Deposit on gold lighter by 1.4 in 10^6.

These results answer the objections of Hering[7] to the use of platinum as the cathode in the voltameter. According to his theory the deposit in the gold crucibles should be the heavier, owing to the reduction of oxygen in the surface of the platinum. In another place we have noted the change in size of the silver crystals, due to saturating the surface of a strip of platinum with oxygen, but the effect on the mass of deposit seems to be negligibly small. Aside from the lower price of gold than platinum, we prefer the latter because of its being more durable.

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[7] Trans. Am. Elec. Chem. Soc., 12, p. 293.

The quantitative work on the second series of experiments was discontinued April 5, 1910, to take part in the cooperative work with the National Physical Laboratory, Physikalisch-Technische Reichsanstalt, and the Laboratoire Central d'Électricité.

II. PREPARATION AND TESTING OF SILVER NITRATE FOR USE IN THE SILVER VOLTAMETER

A. PRELIMINARY WORK WITH COMMERCIALLY PURE SILVER NITRATE

It was early found that the essential differences between the various types of voltameters, especially as regards the different character of septa employed, gave rise to variations in the values obtained, which were independent of the source of the silver nitrate used and which were far greater in magnitude than those arising from the relatively slight amounts of impurities present in commercially pure salt. Consequently no special attempt was made in this part of the work to obtain silver nitrate of the highest degree of purity such as was used later.

Two large lots of silver nitrate crystals obtained from the Gold- und Silber-Scheide-Anstalt, Frankfurt a. M., yielded silver deposits, when electrolyzed, which were nonstriated and markedly crystalline in character, and solutions of this salt in the best twice-distilled water were neutral toward litmus paper as nearly as could be judged.[8] This material was therefore used without further purification in many of the experiments recorded in the present paper. The values obtained with this salt, especially in the small Richards voltameter, are very near the true value, being in good agreement with the later results obtained with recrystallized salt of a very high degree of purity.

B. IMPORTANCE OF CERTAIN CLASSES OF IMPURITIES IN VOLTAMETER WORK

Our earlier investigations of the chemical problems connected with the voltameter had been confined almost entirely to the question of the effect of filter paper, and had revealed the preponderating importance of certain classes of reducing substances as impurities in the electrolyte. The pronounced effects produced in the voltameter by the presence of minute quantities (0.0001 per cent) of certain reducing substances had made it evident that no sample of silver nitrate, however carefully prepared, could be considered suitable for use in voltameter work of the highest precision without being actually tested for these exceedingly slight traces of reducing impurities. Amounts so small may be produced in ways which can not be prevented merely by excluding foreign organic material, because these impurities may be produced by the process of purification itself, as will be shown later. In this connection it must be borne in mind that these reducing impurities are not necessarily of organic origin, but may be formed from pure silver, nitric acid, and water (e. g., hydrazine, hydroxylamine, nitrites, hyponitrites, etc.), or colloidal silver itself may be formed directly from perfectly pure materials by heat or other conditions imposed by the nature of the process.

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[8] See p. 527.

The above considerations hold true in the main of a few other impurities which affect the results in the voltameter, when present in small amounts. This applies especially to colloidal silver hydroxide, which the later work showed could have a pronounced effect upon the weight of the silver deposit when present to the extent of only a few parts per million. Very small amounts of free nitric acid also affect the results, but to a less extent than does the colloidal silver hydroxide. Other impurities which affect the results when present in small amounts are silica and carbon dioxide. These impurities are more easily excluded than the ones just mentioned, however, and relatively larger amounts are required to affect the results. Their influence will be discussed in a subsequent paper of this series.

By far the most difficult problems connected with the preparation of silver nitrate for use in the voltameter have to do with the exclusion or removal of reducing impurities (especially colloidal silver [9]) on the one hand and of "uncombined" acid or base on the other. It was found necessary, therefore, to carefully test all samples of material, however carefully prepared, for these objectionable impurities. The tests employed for this purpose are discussed in the following pages. Methods of purification were finally devised, by means of which these impurities can be excluded with comparative ease, so that it is now a practicable matter to prepare silver nitrate of satisfactory purity for voltameter work.

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[9] See p. 531.

C. TESTS FOR UNCOMBINED ACID AND BASE

1. NECESSARY CONDITIONS FOR THE TEST

It was found necessary, in order to obtain results of the accuracy desired in the voltameter determinations, to define the neutrality of the electrolyte to within a part in a million of "uncombined" acid or base. In this section an account will be given of the method that was developed to meet this requirement.

The test is not designed to determine the absolute concentration of the hydrogen ions, but only to determine whether there is any "excess" or "uncombined" acid or base present. Pure silver nitrate appears to be hydrolyzed to an appreciable extent, as indicated by its behavior toward methyl orange, phenolphthalein, and some other indicators (see Part II, p. 247) and by certain other properties. A brief theoretical discussion of the degree of hydrolysis of this salt in $\frac{N}{2}$ solution is given below.[10] The question as

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[10] The theoretical degree of hydrolysis of $\frac{N}{2}$ $AgNO_3$ may be calculated from the solubility products of AgOH and H_2O. For—

$$\frac{\alpha^2}{(1-\alpha)V}=\frac{k_w}{k_b}$$

where α = degree of hydrolysis;

V = dilution, or number of liters in which 1 gram equivalent is contained. $V=2$ in this case.

k_w = solubility or ionic product of water;

k_b = solubility or ionic product of AgOH.

$k_w=1.2\times10^{-14}$;

$k_b=2\times10^{-8}$.

When hydrolysis is slight,

$$\frac{\alpha^2}{V}=\frac{k_w}{k_b}=\frac{1.2\times10^{-14}}{2\times10^{-8}}=0.6\times10^{-6}$$

$$\alpha=\sqrt{1.2\times10^{-6}}=1.1\times10^{-3}$$

Therefore, theoretically about one-thousandth of the total amount of $AgNO_3$ in solution is hydrolyzed according to the following reaction:

$$AgNO_3+H_2O\rightleftarrows AgOH+HNO_3$$

The actual hydrolysis, of course, is much less than this; probably about 1.3×10^{-6}, as indicated by the intensity of color produced by methyl orange. The concentration was found to be too slight to affect the rate of hydrolysis of cane sugar by as much as 0.1 per cent in one day. Its effect upon the potential of the hydrogen electrode has not been determined. It is our present intention to apply this method at some future time.

to the ideal concentration of hydrogen ions in the electrolyte will be discussed in a later paper.

The usual methods of testing the neutrality of salts do not apply to silver nitrate solutions. Thus, toward litmus silver nitrate solutions react alkaline, even after the addition of 1 part in 100 000 of nitric acid, while the same sample will show an acid reaction toward methyl orange, even after the addition of an unlimited amount of alkali, so long as any undecomposed silver nitrate remains (i. e., so long as the Ag is not completely precipitated as AgOH). (For further details, see p. 247 of Part II of this series.) Toward phenolphthalein silver nitrate solutions show an acid reaction in the absence of carbon dioxide. So far as we are aware, all the data in the literature on the acidity of the electrolyte, except those by Leduc,[11] were obtained by litmus or other similar indicators applied directly in the usual way and can not therefore be relied upon for the reasons just given.

The following method of estimating the "uncombined" acid or base in silver nitrate is free from any uncertainties connected with the exact estimation of the absolute hydrogen ion concentration of solutions of partially hydrolized salts. The standards of neutrality used are the purest water obtainable, and solutions of the chlorides and nitrates of sodium or potassium in this pure water. These standards are as nearly absolute as can be realized experimentally, where a salt solution of some kind is necessary. The indicator chosen was iodeosine.[12] This is an exceedingly sensitive indicator (when used in ether-water solution) and may be readily used in titrating with thousandth normal solutions. The indicator is colorless in acid and pink in alkaline solution. The neutral point is unaffected, even by fairly concentrated solutions of pure sodium or potassium chloride (or nitrate); yet a single drop of a 0.001N solution of acid or alkali added to 10 cc of neutral solution is quite sufficient to cause a pronounced change in color. Its behavior toward acids and bases of different strengths is similar to that of methyl orange. In the present work it has been used only for titrating sodium hydroxide with either sulphuric or nitric acid. It is not necessary to expel the carbonic acid before titration, since the end point is not affected by the amounts ordinarily present.

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[11] This Bulletin, 9, p. 159; 1912.

[12] Förster and Mylius: Zs. anal. Ch., 31, p. 248; 1892.

If the Ag be precipitated as AgCl by means of neutral recrystallized KCl or NaCl solution, and the AgCl filtered off through asbestos, the filtrate shows a neutral reaction toward all indicators if the original $AgNO_3$ contained no "uncombined" acid or alkali. Samples of silver nitrate purified by repeated recrystallization have been obtained which show a practically neutral reaction toward iodeosine when tested in this manner, *whereas if so little as one part in one million of nitric acid (or alkali) be added to the original solution*, it can be detected in the filtrate from the precipitated AgCl. In testing for amounts of acid less than several parts in one hundred thousand the AgCl must be filtered off by means of asbestos or finely divided platinum instead of filter paper, for the reason that pure distilled water extracts a small amount of oxycelluloses and cellulose hydrates from filter paper which show basic reaction toward iodeosine and methyl orange.

2. PREPARATION OF REAGENTS.

Iodeosine Solution.—About 500 cc of ordinary ether is shaken up with one-tenth its volume of dilute sodium hydroxide solution (5 per cent) in a separatory funnel, and the aqueous layer run off. The ether is then washed two or three times with distilled water in the same manner, using about one-tenth its volume of water each time. From 2 to 5 mg of iodeosine is dissolved in this washed ether. The solution is kept in a glass-stoppered bottle in contact with about one-tenth its volume of water. On long standing (two or three weeks) the iodeosine decomposes to a considerable extent. This is indicated by a diminution in its sensitiveness toward 0.001 N acid or base. A fresh solution should then be prepared.

Potassium Chloride Solution.—Prepare a 10 per cent solution from pure recrystallized potassium chloride and "conductivity" water. This solution should show an approximately neutral reaction toward iodeosine (the amount of base or acid, expressed in terms of HNO_3, should not exceed one part in a million).

Thousandth Normal Nitric Acid and Thousandth Normal Alkali.—Prepare by diluting 0.1 N or 0.01 N solutions that have been standardized in the usual way. It is not necessary to exclude carbon dioxide. Fresh solutions should be prepared from time to time on account of the solubility of the glass containers.

3. DETAILS OF THE TEST FOR ACID OR BASE

10 cc of the silver nitrate solution to be tested is measured into a 100 cc beaker by means of a pipette or graduate, and just enough of the KCl solution added to completely precipitate the whole of the silver as silver chloride. This precipitate is removed by means of a filter of asbestos or finely divided platinum. If asbestos is used, *any appreciable excess of KCl solution must be avoided* since it reacts with the asbestos, forming acid salts which appear in the filtrate. (The potassium nitrate formed in the precipitation of the silver chloride has no such action upon the asbestos.) Not more than from 3 to 5 drops of KCl solution in excess of the amount required to exactly precipitate the whole of the silver as silver chloride should be used.

If the acidities are more than about 1 part in 100 000, the amount of acid left adhering to the precipitate and the filter mat can not be neglected. Either of two procedures may be followed—(1) the precipitate and filter mat may be washed two or three times with a small volume of neutral water, so as to recover all the acid and the titration then made with the total volume of the filtrate; (2) 10 cc of the filtrate may be taken (without washing the precipitate and filter mat) and a correction applied for the difference in volume between 10 cc and the total volume before filtration. These two methods have been found to agree in practice.

Before use, the filter and all glass vessels should be tested as to their effect upon the neutrality of "conductivity" water. This is done by determining the basicity (or acidity) of the water before and after contact with the glass vessels or filtration through the filter. Good conductivity water (conductivity less than 1.5×10^{-6}) from final distillation from alkaline permanganate is usually basic to the extent of about 0.6 parts in a million, as determined by titration with 0.001 N acid, using iodeosine indicator in the manner described below. The change in basicity caused by filtration or contact with glass vessels (for the time usually occupied in a regular determination) should not exceed 0.3 parts in a million.

The titration is carried out in a 25 cc glass stoppered cylinder of resistant glass in the following manner: Two cc of distilled water and 4 to 10 cc of the ether solution of iodeosine are first placed in the cylinder. This aqueous-ether solution is neutralized by the addition of 0.001 N acid or alkali until 1 or 2 drops of the 0.001 N solution is sufficient to change the solution from colorless to a very distinct pink, or vice versa, after vigorous shaking. If this change is not sharp, it indicates that not enough iodeosine is present in the ether solution or that the iodeosine has partially decomposed, in which case a fresh solution should be prepared. Ten cc of the solution to be tested is now added to this *neutral* solution of the indicator and neutralized by the addition of 0.001 N acid or base. Or, if preferred, 40 or 50 cc of the ether solution may be neutralized in a stoppered cylinder and used as required. Each cc of the 0.001 N solutions contains 0.000063 g in terms of nitric acid. Hence, for a 10 cc sample, the number of parts per million in the solution tested is given by multiplying the number of cc of solution required for neutralization by the factor 6.3. The value thus obtained is corrected for the amount of acid or base present (if any) in the known volume of KCl solution used. This value for the KCl solution must be determined before and after each series of determinations, since it tends to become slowly more basic, due to its action on the glass container. If the asbestos or glass vessels are shown to be appreciably soluble by the test with conductivity water, already described, correction for the amount of base (or acid) so dissolved must also be applied by making a blank determination with conductivity water, using the same volume as used in a regular determination and allowing the same time of contact with the vessels and filter. The solubility of the vessels and asbestos filter is usually so very slight in the time required for a determination that it can be entirely neglected; if it is appreciable, more resistant glassware should be obtained. If asbestos is used for filtering, 5 cc of the KCl solution and 10 cc of *neutral* double-distilled water is added directly (without filtration) to the neutral aqueous-ether solution of the indicator in the titration cylinder;

the amount of 0.001 N solution required for neutralization does not usually exceed 0.1 cc (if more than this is required, the KCl is unfit for use and a more nearly neutral sample of recrystallized KCl should be prepared).

D. PERMANGANATE TEST FOR COLLOIDAL SILVER AND OTHER REDUCING IMPURITIES IN SILVER NITRATE

1. OBJECT OF THE TEST

In the early part of present investigation (July, 1909) the behavior of various electrolytes toward thousandth normal permanganate solution was investigated in the hope that it would afford some clue as to the cause of the marked differences in the results obtained with the various types of voltameters then in use. It was suspected that these discrepancies were in some way connected with the presence of impurities of a reducing nature formed either by the action of organic septa or possibly by secondary reactions at the anode as postulated by Richards, Collins, and Heimrod.

Further development of this test resulted in a method of detecting these highly objectionable reducing impurities that proved to be far more sensitive and of much wider application than had been expected from it at first.

The greatest value of the permanganate test is in detecting minute traces of colloidal metallic silver which may be formed in the process of fusing pure silver nitrate even when this is done with great care. We know of no other test which is so sensitive for this purpose. This test, together with the neutrality test described in the preceding section, has made it possible to specify a standard degree of purity of fused silver nitrate for use in the voltameter. As will appear later, this can not be safely done by fixing the conditions of fusion in respect to temperature, time of fusion, etc.

The test has also been of great use in estimating the degree of contamination of commercial samples of silver nitrate with organic material.

2. PREPARATION OF SOLUTIONS

Thousandth Normal Permanganate Solution.—Dissolve 0.0316 g of crystals of potassium permanganate in distilled water and dilute to 1 liter. This solution may be standardized by comparison with standard sodium oxalate. The solution is best preserved in the dark, and should be kept free from contamination with dust or organic material.

Concentrated Nitric Acid.—The best grade of commercial c p acid is satisfactory. It should be tested for reducing impurities as follows: 1 cc of the concentrated acid is diluted to 10 cc with double-distilled water (in glass-stoppered cylinder) and 1 cc of 0.001 N permanganate solution added; the pink color should persist for 20 minutes or longer. The concentrated acid must be kept in the dark or in a brown bottle and preferably in a cool place.

3. METHOD OF MAKING THE TEST

The test with permanganate is made as follows: 10 cc of a 66.6 per cent solution of the $AgNO_3$ to be tested is placed in a glass-stoppered cylinder of 25 cc capacity and acidified by the addition of 1 cc of concentrated nitric acid (free from reducing substances). After thorough mixing of the acid and solution, 0.5 cc of the 0.001 N permanganate is added and the whole again shaken to mix the solutions. The time required for the pink color to fade is noted. After the solution is colorless a second half cubic centimeter of the permanganate solution is added as before. The addition of the permanganate is continued in portions of one-half cubic centimeter until the color persists undiminished in intensity for five minutes or longer.

4. TESTING FOR ORGANIC IMPURITIES

For the detection of the more resistant forms of organic reducing impurities (principally cellulose hydrates from filter paper) the acid silver nitrate crystals should be first fused. The more reactive reduction products thus formed (principally colloidal silver) readily reduce permanganate. The amount of these more active reduction products formed (even from very resistant organic material) is sufficient to render the test a very sensitive one for the detection of organic material in general.

The reliability of the "fusion-permanganate test" as a means of detecting the presence in silver nitrate of reducing impurities not otherwise capable of detection by any method yet employed (except perhaps the "volume effect" in the voltameter) is illustrated by the following tests (Table 14) applied to solutions containing *known amounts of cane sugar and filter paper extract* (*oxycelluloses*). It will be seen that except where the silver separated in "massive condition" the "permanganate numbers" are approximately proportional to the amounts of organic material added and that exceedingly small traces can be detected in this way. The salt used was recovered from used solutions by evaporation and recrystallization from 10 per cent HNO_3 solution. The crystals were centrifugally drained and were, of course, strongly acid. After fusion in the manner described 10 cc of a 66.6 per cent solution required only 1 cc of thousandth normal permanganate to produce a color which persisted for longer than one-half hour. In the table, by "permanganate number" is meant the number of cubic centimeters of thousandth normal permanganate reduced by 10 cc of a 66.6 per cent solution of the fused silver nitrate, the fusion and test being made in the manner described. The filter paper extract was prepared by digesting about 3 g of Schleicher & Schull No. 597 filter paper in 25 cc of distilled water at 30° C for 10 minutes and filtering through a sheet of the same paper. Measured volumes of a standard solution of the impurity was added to a definite volume (30 cc) of a 66.6 per cent solution of the silver nitrate and the mixed solution was evaporated to dryness in a 50 cc platinum dish on the steam bath and then fused in the same dish.

TABLE 14

Amount and kind of impurity added	Permanganate number after fusion	Remarks
1 cc of filter paper extract	3.5	
2 cc of filter paper extract	5.0	
5 cc of filter paper extract	12.5	
0.1 cc of 0.5 per cent solution of cane sugar	3.0	
0.5 cc of 0.5 per cent solution of cane sugar	8.0	
1 cc of 0.5 per cent solution of cane sugar	13.0	Considerable gray metallic silver separated
5 cc of 0.5 per cent solution of cane sugar	35.0	Most of the silver separated as the ordinary gray metallic variety (non-colloidal)

It is not claimed, of course, that the organic material is *completely* oxidized to carbon dioxide (or carbon monoxide) and water, but the partial oxidation is sufficient to render the method very sensitive indeed as a means of detecting the presence of traces of organic reducing material. Thus, less than 0.001 per cent of cane sugar can be readily detected in this way; this corresponds to 0.0001 per cent in a 10 per cent solution of the salt. This, of course, is much more sensitive than any method of direct combustion would probably prove under the conditions, besides possessing very great advantages in the matter of expediency and simplicity. We have not yet definitely shown that the test is of universal application to all classes of organic substances, although it is capable of revealing very small amounts of even such a difficultly oxidizable substance as paraffin, so that it seems highly probable that no appreciable amount of organic material of any kind could escape the test. Certainly any reducing material sufficiently active to produce any reducing action upon silver nitrate solution could not possibly escape detection by this test. This is illustrated by the case of cane sugar mentioned above, for this substance has practically no reducing action whatever on silver nitrate solutions (Part II, p. 252); yet if silver nitrate containing traces of it be fused, sufficient colloidal silver is formed to enable it to be readily detected by the permanganate test. This test, together with the iodeosine test for "neutrality," has been a very important factor in increasing the *reproducibility* of the voltameter, the results being independent of the *source* of the material. Likewise the two tests mentioned have enabled us to obtain concordant results with silver nitrate purified by two different methods, (1) by recrystallization from faintly acid solution, (2) by recrystallization from strongly acid solution followed by fusion.

5. TESTING FOR COLLOIDAL SILVER

The following test shows the reliability of the permanganate test as a method of accurately estimating the amount of colloidal silver present in silver nitrate.

A colloidal silver solution prepared by Bredig's method (using conductivity water of the highest purity) was titrated first against a standardized solution of ammonium sulphocyanate, and then an equal volume of the same solution was titrated against thousandth normal permanganate in the usual manner, allowing five minutes for the pink color to discharge itself. The agreement between the values was well within the experimental error.

25 cc of Bredig's silver hydrosol required 0.4 cc of $\frac{N}{100}$ NH_4CNS solution.

25 cc of Bredig's silver hydrosol required 3.75 cc of $\frac{N}{1000}$ $KMnO_4$ solution.

The calculated equivalent of 0.4 cc of $\frac{N}{100}$ NH_4CNS is 4 cc of $\frac{N}{1000}$ $KMnO_4$. The agreement would probably be closer with thousandth normal NH_4CNS solution instead of hundredth normal.

By titrating concentrated solutions of silver nitrate (60 to 70 per cent) with thousandth normal permanganate less than 0.001 per cent of colloidal silver may be detected in this manner.

As prviously stated, the test is particularly applicable to the detection and estimation of colloidal silver formed by "overfusion" of silver nitrate. That the reducing substance formed in this way is colloidal silver and not subnitrate is indicated by the appearance of solutions of the fused salt when examined under the ultramicroscope; the presence of colloidal particles is readily revealed in this way. Colorimetric estimation of the nitrites present in such fused salt shows that these are not present in amounts sufficient to account for an appreciable proportion of the permanganate reduced.

The permanganate test is equally applicable to the detection of reduced colloidal silver in recrystallized silver nitrate.

In testing recrystallized salt it is always advisable to test a portion of it with permanganate both before and after fusion. The test before fusion will indicate whether the process of recrystallization has been properly carried out, and the test upon the fused salt will reveal the presence of any organic material which may by accident have found its way into the material. In our further investigations no silver nitrate has been used in the voltameter without first being tested in this way. In addition great care was of course exercised in protecting the material from dust and other sources of contamination with organic material.

II. DISTILLATION AND TESTING OF THE WATER

1. METHOD OF DISTILLATION

The water used in making the electrolyte for the voltameters has been twice distilled. It has always been free from suspended matter and carefully kept in large stoppered bottles of resistant glass that have been in use for some years and now produce very little effect on the conductivity of the water. The method of preparing the water has been as follows: Water from the city mains, having a conductivity of about 3×10^{-6}, is passed directly through an automatic regulator into a large block tin still having a daily capacity of 75 liters. The water is boiled by steam at 40 pounds pressure, passing through a coil in the container of the still. Before reaching the condenser the vapor passes through a bed of quartz to remove any particles of matter that might be carried over mechanically. After condensation the water is collected in a large glass carboy. The conductivity of this is from 3 to 6×10^{-6}.

The second distillation takes place in another still of smaller capacity. The first distilled water is rendered alkaline and potassium permanganate added before being put into the second still. Heat is supplied by steam under pressure as before. The water vapor passes through traps to catch any matter carried over mechanically, and then is condensed in block tin. The water is collected in a large glass receiver with a guard tube of soda lime and H_2SO_4. A considerable fraction of the distilled water is discarded at the beginning and end, only the middle portion being saved. Tests for ammonia are always made with Nessler's reagent, and from time to time we have made conductivity tests also. The conductivities have ranged from 0.85×10^{-6} to 2×10^{-6}, but were usually about 1.3×10^{-6}.

2. REQUIREMENTS AS TO CONDUCTIVITY, ALKALINITY, ETC.

As we lay great stress on the necessity for purity of the electrolyte in the silver voltameter, it is axiomatic that only the best water should be used. This precaution becomes of especial importance, because the impurities which increase the conductivity of the water are usually alkalis. We have found that alkali in the electrolytes, although not present in sufficient amounts to show a precipitate, will nevertheless increase the deposit of silver and in some cases alter slightly the appearance of the deposit. We have measured the conductivities of distilled water containing known amounts of impurities and conclude that for work of the highest precision the water should not have a greater conductivity than 2.5×10^{-6}.

It sometimes happens that when neutral $AgNO_3$ is used the resulting solution will show a slight trace of alkalinity when tested with iodeosine, which is due to the alkalinity of the water itself. In some instances we have rendered such electrolytes slightly acid by the addition of pure nitric acid, but more recent tests have shown that this is a doubtful procedure. This is due to the fact that alkaline water absorbs or combines with larger quantities of carbon dioxide from the atmosphere than neutral water and the mere addition of acid does not, of course, expel the gas (unless the solution is boiled). We have found that free carbon dioxide in the electrolyte in some manner greatly increases the weight of silver deposited in the voltameter; consequently any procedure which tends to increase the normal amount of carbon dioxide which is unavoidably retained by the electrolyte (when working in an atmosphere of ordinary air) must be carefully avoided. The water should therefore be as nearly neutral as possible as it comes from the still. In testing the neutrality of the water a neutral solution of iodeosine in the ether-water mixture is prepared as described on page 529 and 10 cc of the water to be tested added to this and the titration made with thousandth normal acid or alkali as in testing any other solution.

The question as to the manner in which the carbon dioxide increases the weight of the electro-deposited silver will be given attention in a subsequent article.

F. STANDARD METHODS FOR THE PREPARATION OF SILVER NITRATE FOR USE IN THE VOLTAMETER

1. SOURCE OF MATERIAL

The methods of purification described on the following pages are intended to be applied only to silver nitrate, which is already of a fair degree of purity. Preferably it should conform to tests such as are given in any of the good manuals on the purity of reagents. Most of the c p or "analyzed" salt obtained from the best manufacturers is satisfactory material with which to start. Of course any one of the special methods to be described may be repeated as often as desired, or until there is no further change in the values obtained in the voltameter; but in case the material does not conform to the tests referred to above it will save much labor first to recrystallize the salt from strongly acid solution until it does meet these requirements except as to neutrality and then remove the acid by one of the special methods of purification to be described.

If the salt is prepared from metallic silver and nitric acid, the excess acid must be removed either by the method of recrystallization or by fusion, both of which processes are described in detail below.

1. PURIFICATION BY RECRYSTALLIZATION

The very sensitive iodeosine test for uncombined acid and base, described in section C, shows that salt obtained by recrystallization from *neutral* water is slightly basic. This is especially true if fairly dilute solutions are concentrated by evaporation (even under diminished pressure) in order to cause a separation of crystals.

The formation of faintly basic crystals has been observed when quartz vessels were used and when every precaution was taken to insure the purity and especially the neutrality of the water. The amount of base present in crystals so prepared as determined by the iodeosine test has never been found to exceed two parts per hundred thousand in the solid salt or two parts per million in 10 per cent solution. Notwithstanding the fact that this trace of base may be negligible for most work, even of an exact nature, it can not be disregarded in work with the silver voltameter, because it gives rise to the "volume effect" which has been observed with electrolytes known to be contaminated with filter paper, added base, etc. In recrystallizing there is also a tendency for the salt to become slightly reducing in character (unless traces of acid are present). This is brought about by heating the solution. The greater part of the trouble experienced in the earlier work with salt recrystallized from neutral solution was probably due to the basic reaction of the crystals rather than to reducing impurities.

If the recrystallization is carried out with faintly acid solutions and the crystals drained until they are either exactly neutral or faintly acid (a few parts per 100 000), the process may be repeated until the salt does not show the "volume effect" and does not reduce permanganate. (See p. 516.)

Regulating the acidity of the solution so that the drained crystals are not basic, on the one hand, nor too strongly acid, on the other, is often rather difficult. Moreover, the yield of crystals is ordinarily not much greater than half of the salt taken. For these reasons it was found more convenient and more economical to first crystallize from strongly acid solution (10 per cent or more) and then expel the acid by fusion in the manner described in section G. *This was done, however, only after it had been found that the fusion process when properly regulated yields salt which gives the same results in the voltameter as the recrystallized salt.*

A solution which is neutral toward iodeosine remains neutral after heating at the temperature and for the length of time usually required in recrystallizing, yet the crystals obtained when the same solution is allowed to cool will show the basic reaction referred to above. This indicates that while the heating process may produce silver hydroxide (or basic silver nitrate), the equivalent amount of acid still remains in solution, and therefore after precipitating and removing the silver as silver chloride, the filtrate is still neutral toward iodeosine. This behavior, in our opinion, is due to a very slight hydrolysis of silver nitrate (p. 526) which is favored by the higher temperature. It is probable that the silver hydroxide (or basic nitrate) formed by hydrolysis at the higher temperature becomes colloidal and separates with the crystals.

The important requirement in purifying silver nitrate entirely by recrystallization is to have the mother liquor of the *final* crystallization sufficiently acid to prevent the crystals from becoming basic, but not sufficient to cause them to become too strongly acid for use in the voltameter (i. e., the crystals must not contain more than a few thousandths of 1 per cent of acid). The maximum acidity of the mother liquor that is permissible in the final crystallization depends a great deal upon the efficiency of the means used for draining the crystals, but is about 1 per cent for the most efficient centrifugal draining. On the other hand, the minimum concentration of acid that will prevent the formation of basic crystals is approximately 0.1 per cent of the water used as solvent, although this also depends to some extent upon the temperature to which the solution is heated and upon the time of heating. The temperature should be regulated between 100° and 110° C (the boiling point of concentrated solutions is above these limits), and the time required for disintegrating the crystals ought not to exceed two hours. Crystallization by evaporation even at ordinary temperatures in vacuo does not, however, in our experience, prevent the crystals from becoming faintly basic when separated from perfectly neutral solution.

Best results have been obtained by recrystallization from solutions made acid to the extent of 0.5 per cent of the water used and draining the crystals obtained by means of a porcelain centrifuge, having a rotating basket approximately 15 cm in diameter and using 1200 r. p. m.[13]

The salt used in preparing electrolyte E (Report to International Committee, p. 158) was prepared in this way and contained 0.003 per cent nitric acid and showed no volume effect or permanganate reduction either before or after fusion. Data concerning various electrolytes from recrystallized salt prepared in this manner will be given in Part IV of this series. It was found that salt recrystallized first from 10 per cent nitric acid solution (with centrifugal draining) and then from neutral twice-distilled water contained just about the right amount of acid for use in the voltameter (i. e., from 0.001 per cent to 0.003 per cent of the solid salt).

All but the final crystallization may, of course, be made from strongly acid solution. This is advisable, not only because of the greater yield obtained, but also because it seems to facilitate the removal of reducing impurities, so that fewer crystallizations are required to give a satisfactory product.[14]

The crystallization is carried out in porcelain, quartz, or platinum vessels. No differences have ever been observed in the results obtained with salt crystallized in vessels made of these several materials. We prefer porcelain vessels, since they are obtainable in a larger assortment of convenient sizes and shapes; and because of their lower cost one need not be handicapped by having to work with a limited number.

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[13] If a centrifuge is not available, the draining may be accomplished by means of a porcelain funnel with perforated draining plate fitted to an ordinary filtering bottle, which has been thoroughly leached out. In fact, a preliminary draining by this means is a helpful adjunct to centrifugal draining, especially if the solution has been cooled to increase the yield of salt, since the main portion of mother liquor can be quickly removed by this means before it has had time to dissolve more salt in warming to room temperature.

[14] If the salt is strongly contaminated with filter paper or other organic reducing material, a preliminary fusion until it begins to darken and is slightly basic lessens the number of crystallizations necessary.

In dissolving crystals of silver nitrate it is best to heat the solution over a steam bath. A free flame should not be used. In some cases we have heated the beaker containing the solution in a cylindrical-shaped vertical electric furnace of sufficient depth to permit of the heating of the solution uniformly for about one-half its depth. The temperature was kept at about 120° C. The upper portion of the beaker should be protected from radiated heat by means of a sheet of asbestos provided with a circular opening to admit the beaker.

The yield from a single crystallization is greatly increased by cooling the mother liquor with an ice bath or freezing mixture, provided the crystals are immediately drained before they have time to redissolve as the solution warms up to the temperature of the room.

In crystallizing from strongly acid solution the yield may be further increased by adding the acid after the crystals have been dissolved in neutral water and before the solution has cooled sufficiently to cause a separation of the crystals. Addition of the acid causes an immediate separation of the larger portion of the salt in the form of very fine crystals. In this form they are more readily freed from excess nitric acid by draining.

3. PURIFICATION BY RECRYSTALLIZATION FROM NITRIC ACID FOLLOWED BY FUSION

The salt should first be recrystallized from strong nitric acid solution in the manner described in the preceding section and the process repeated until 10 cc of a 66.6 per cent solution of the well-drained crystals reduces not more than 1 cc of thousandth normal permanganate solution.

The crystals are then fused under conditions which insure the retention of a few thousandths of 1 per cent of the acid. The conditions of fusion which have been found to give the best results are described on page 549.

Ordinarily the product thus obtained will not have a permanganate number greater than two and will not show the volume effect or any other evidence of contamination with objectionable impurities. If the product reduces more than this amount of permanganate or shows other evidence of the presence of impurities, the salt must again be recrystallized from strongly acid solution and fused again in the same manner. This treatment (alternate crystallization and fusion) must be repeated until the final fused product conforms to the following requirements:

(*a*) It must contain not more than two parts nor less than 0.5 part of nitric acid in one hundred thousand parts of solid salt (or in one million parts of a 10 per cent solution). It is not difficult to realize this requirement if the fusion is carried out as described on page 549, since the process of fusion expels all but about this amount of acid.

(*b*) A 10 cc sample of a 66.6 per cent solution must not decolorize more than 2 cc of 0.001 N permanganate solution, the permanganate being added one-half cubic centimeter at a time and five minutes allowed to elapse after the addition of each portion.

Before dissolving the fused salt (in preparing the electrolyte) the surface is washed by placing the solid cake in a funnel and quickly pouring sufficient water over it to remove a thin outer layer of the salt. This addition to the process of preparing the electrolyte was suggested and first used by Mr. F. E. Smith of the National Physical Laboratory. The object was to remove any possible traces of dust or other impurities which may have collected on the surface. We have found that in cases of *badly contaminated silver nitrate* this washing process also sometimes removes a considerable portion of the reducing substances (probably finely divided metallic silver or coagulated colloidal silver) which is found to accumulate on the surface. This is indicated by the fact that in some such instances we have observed that these surface washings reduce appreciable amounts of thousandth normal permanganate, whereas the washings from the interior of the fused cake may reduce much less permanganate than that from the surface. For this reason washing the surface may sometimes shorten the purifying process. The chief value of the process of fusing the salt, however, lies in the aid it gives in quickly removing the excess acid and more important still, the very sensitive and convenient means it affords in connection with the permanganate test, of *detecting the presence of colloidal silver and also any reducing impurities* which are so objectionable in voltameter work.

4. PURIFICATION OF USED SOLUTIONS

In preparing pure silver nitrate from old used solutions, especially those strongly contaminated with filter paper or which had been stored in glass containers for several months, we have in some cases evaporated the solutions completely to dryness in porcelain vessels, and subsequently fused until the melt darkened slightly. This treatment decomposes any organic reducing material present and renders most of the silica, iron, etc. (from the glassware) insoluble.

The solid was then dissolved in hot distilled water without the addition of acid and filtered through asbestos to free it from the greater portion of silica and insoluble oxides. This material when crystallized from 10 per cent nitric acid solution, centrifugally drained in a porcelain centrifuge and fused, usually gave a satisfactory product; if not, it was recrystallized from 10 per cent nitric acid, drained, and fused again. This second treatment has always yielded a satisfactory product.

If the solution is not too strongly contaminated, the mother liquor may be evaporated again and a second crop of crystals obtained, or, as suggested by Mr. F. E. Smith, it may be used as a solvent for other salt to be purified in the same manner.

5. PROTECTION FROM DUST

During all the processes of preparing the salt, it was protected from any appreciable contamination with dust by means of cover glasses or inverted crystallizing dishes, which were kept over the salt or solution except when the transferring of the salt from one container to another prevented, and even in these cases a large cover glass was held above the vessels and between the operator and the material. We have never observed, however, that short exposure to the usual conditions of the atmosphere (provided it is free from fumes) has in any way affected the properties of the salt as shown by the chemical tests described (neutrality and reducing properties) or by the values obtained with the voltameter, and therefore believe this is only a minor source of contamination as compared to those discussed at the beginning of this chapter.

G. FUSION OF SILVER NITRATE

1. EFFECT OF PROLONGED FUSION AT TEMPERATURES NEAR THE MELTING POINT

The first fused silver nitrate prepared in the present work was fused under conditions which were, as nearly as practicable, the same as described by Richards and Forbes[15] in their work on the atomic weight of nitrogen. The salt was prepared by dissolving very pure metallic silver in redistilled nitric acid. Several samples of silver from different sources were used and led to the same results.

The product obtained did not, however, prove satisfactory for voltameter work, since it reduced appreciable amounts of thousandth normal permanganate (14 g reducing from 3 to 4 cc), and in 50 per cent solution even *gave a striated deposit when electrolyzed.* It was therefore concluded that the acid could not be completely expelled by fusion without slightly decomposing the salt into metallic silver, which, of course, is to be avoided above all other impurities in voltameter work.

At the time these fusions were made the iodeosine test for neutrality had not been fully developed, and we had not yet discovered that fusion for a much shorter time suffices to remove the free acid (although not all the moisture and air). The fusion method was therefore abandoned for the time and recourse had to the method of recrystallization.

While it appeared possible that these unsatisfactory results might have been due to failure on our part to exactly duplicate the conditions described by Richards and Forbes, it was apparent that if this were so the *limits* within which the conditions could be safely varied must be very narrow; too narrow, indeed, to render the process free from grave danger of introducing contaminations into the electrolyte.

It seems that no such narrow limitations apply to the method of fusing, if the sole object is to determine the mass of the salt for purposes of atomic weight work. This was admirably demonstrated by Richards and Forbes, who showed that the salt could be kept in a fused condition at 210° C for several hours longer than the usual time which they employed without suffering loss in weight, or it could be redissolved, evaporated, and fused again

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[15] J. Am. Ch. Soc., 29, p. 808.

without undergoing any change in weight which was sufficient to affect their results. In such cases [16] the salt sometimes became slightly darkened, yet without suffering significant loss in weight. On the other hand, it has been observed many times in the present investigation that if fused salt is discolored, even only slightly, it will give a *pronounced* volume effect and will yield a striated deposit with the accompanying high value for the electrochemical equivalent of silver. This is due to the *magnified* effect produced by mere traces of reducing impurities (and colloidal silver) in the voltameter.

It does not seem necessary to further describe the conditions of fusion in this earlier work in which the attempt was made to duplicate the conditions of Richards and Forbes, except to state that great care was exercised in excluding all organic material and special precautions were taken to have the temperature of the oven uniform in order that the actual temperature at which the fusion was carried out could be accurately determined. The only conditions differing from those described by Richards and Forbes that were knowingly altered consisted in the use of a quartz evaporating dish instead of the quartz flask used in their work. This was done because a quartz flask was not available at the time. When the evaporating dish was used, the salt was protected from dust by means of an inverted funnel clamped in position just above the dish; the stream of dry and dust-free air entered through a delivery tube which passed through the funnel stem. The circumstance that in the present work it was not necessary to carefully guard against loss of silver by spattering simplified the procedure enormously. The unsatisfactory behavior in the voltameter of salt fused *under these conditions* has already been described.

2. FACTORS THAT INFLUENCE THE DECOMPOSITION OF SILVER NITRATE WHEN FUSED

Whether silver nitrate is decomposed by heat when fused seems to depend less upon the temperature than upon the amount of acid retained by the melted salt. As soon as the last trace of acid is expelled the salt begins immediately to decompose into silver oxide and colloidal metallic silver. This is indicated by the basic reaction of the salt toward iodeosine (after precipitating the silver as chloride with neutral potassium chloride) and its reducing action upon thousandth normal permanganate. If a trace of acid is retained by the salt, or if, as happens only rarely, it shows an exactly neutral reaction, the product does not reduce appreciable amounts of permanganate and shows no "volume effect" (p. 514).

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[16] J. Amer. Chem. Soc., 29, pp. 814–815. We have obtained the same results.

In all cases, salt which after fusion was found to reduce appreciable amounts of thousandth normal permanganate also showed a faint basic reaction (except when it contained organic material, in which case it always showed unmistakable evidence of reduction to metallic silver, even though the fusion were carried out in such a manner that the fused salt retained quite appreciable amounts of uncombined acid). Fused salt which showed no evidence of such reduction was usually faintly acid (containing from 0.0005 per cent to 0.005 per cent), but occasionally was exactly neutral, or, in a few instances, faintly basic.[17] In the latter case evidently a portion of the salt had been decomposed into silver oxide which had not yet undergone further decomposition into metallic silver and oxygen.

After the last traces of nitric acid have been expelled the rate of decomposition depends chiefly upon the temperature. If the temperature is kept within 2° or 3° of the melting point, which is approximately 208° C., the rate of decomposition is so slight that, as shown by Richards and Forbes, the salt may be kept in a fused condition for an hour or longer without suffering appreciable loss in weight. However, our own results show that the amount of metallic (colloidal) silver formed under these conditions may amount to as much as 0.002 per cent. At 10° to 20° above the melting point the rate of decomposition is probably more than twice as rapid as at its melting point (see p. 548), although, according to some preliminary tests, the loss in weight, even under these conditions, does not seem to be appreciable. But the amount of decomposition as determined by the permanganate and iodeosine tests has been determined under these and several other different sets of conditions (see p. 548), and it is quite appreciable under the conditions last mentioned. It is our belief, therefore, that quite appreciable decomposition can *take* place without a corresponding loss in weight, due perhaps to the retention by the salt of some of the gaseous products of decomposition.

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[17] See Table 15, p. 548.

Salt which has been fused at 230° C. and removed as soon as melted, although neutral, still contains quite appreciable amounts of moisture, dissolved air, etc., as is indicated by the fact that further fusion at the lowest possible temperature causes a relatively large decrease in weight; sometimes this loss is as much as 0.02 per cent, and yet the decomposition as shown by the permanganate test is *nil* in comparison. This shows the necessity of longer fusion, if the mass of the pure salt is to be determined accurately for atomic weight determinations, although it is certainly objectionable if the salt is to be used in voltameter work of the highest precision. After it was found that practically every trace of acid is expelled as soon as the salt is completely fused and that no other sources of error are involved, the method of expelling the excess acid by fusion (instead of recrystallization) was employed almost exclusively because of its greater convenence and economy. Also it is much easier by this method to prevent the formation of basic salt (or oxide) than when the acid is removed by recrystallization. If the crystals are strongly acid, the time required to completely melt the salt apparently has very little effect upon the amount of acid retained; this is no doubt due partly to the fact that the temperature does not rise appreciably above the melting point of the salt until all of the solid has melted; but the principal reason is doubtless due to the gradual liberation of nitric acid included in the crystals as they slowly melt.

The following instances are given in tabular form and will serve to illustrate the effect of the various conditions of fusing, both upon the amount of acid retained and also upon the permanganate reduction shown by the various samples. These are but a few instances chosen from a very large number of cases in which not all of the conditions were made a matter of record, but in which the same effects of the various conditions have been repeatedly observed with samples of salt which the various tests (including the volume effect in the voltameter) showed to be free from reducing impurities. So far as our own experience goes we have not yet succeeded in keeping 100 g of salt or less in a state of fusion for longer than 15 minutes at a temperature of 230° (or more) without its becoming slightly basic. At the same time silver nitrate so fused has always shown permanganate reduction, whereas the same sample fused in such manner as to retain a slight amount of acid will show no such reduction. The limits of temperature and time of fusion within which the fusion may be made with reasonable safety are fairly wide. This is illustrated in part at least by the table given below. But the only safe procedure is to test *in every case* the fused salt, in order to be certain that it is slightly acid or at least that it is not basic, and that it does not reduce appreciable amounts of thousandth normal permanganate.

TABLE 15

Acidity Tests on Fused Silver Nitrate

[The acidity of the salt before fusion was about 0.1 per cent. Acidities after fusion are expressed in parts per million.]

Experiment No.—	Mass of salt fused	Temperature of oven	Time left in oven after completely fused	Acidity after fusion		Permanganate number after fusion	Remarks
				Acid	Basic		
	g	°C	min				
1	16	345	0.5	....	1.5	1.0	Fused in 50 cc platinum dish
2	14	520	1	....	2.0	6.5	Do.
3	14	345	2	....	1.0	2.5	Do.
4	28	295	3.5	....	1.0	2.0	Fused in 20 cc platinum crucible
5	30	318	1	0.3	....	1.0	Fused in 50 cc quartz dish
6	30	230	30	....	2.0	5.0	Do.
7[18]	15	230	15	....	1.6	3.0	Do.
8	15	230	15	0.6	....	1.0	Conditions same as in (7), except that fusion was made in 10 cc quartz test tube
9	15	230	30	0.5	....	1.0	Fused in quartz flask of 50 cc capacity having neck 13 mm in diameter
10	15	230	30	....	2.5	3.0	Fused in same flask as in (9), but with current of purified air flowing over surface of salt
11	15	250	60	....	3.0	6.0	Fused in quartz dish (50 cc)
12	15	345	2	....	1.6	4.0	Do.
13	100	350	0.5	....	4.0	2.0	Fused in 175 cc platinum dish
14	100	350	0.5	....	2.0	2.0	Do.

[18] Dried at 150° C for 15 minutes.

3. STANDARD CONDITIONS FOR FUSING SILVER NITRATE FOR USE IN THE VOLTAMETER

The most important condition to be observed in fusing silver nitrate for use in the voltameter is the maintenance of slightly acid condition throughout the process. The retention of acid in the melted salt whereby slight decomposition is avoided is accomplished by shortening as much as possible the time the salt remains in the fused condition and by reducing the rate of evaporation of acid from the surface of the fused salt.

The first of these objects has been accomplished in the main by removing the salt from the oven as soon as completely fused. Also it has been found practicable to fuse the salt at considerably higher temperatures than the melting point, thus shortening the time of fusion. The temperatures ordinarily employed have been between 250° and 300° C. There is no danger due to superheating at these temperatures when the salt is removed as soon as melted. The evaporation of acid is diminished by decreasing the surface relative to the mass of salt as much as practicable (i. e., deep vessels are used) and by dispensing with the current of air used by Richards and Forbes.[19]

Our best results have been obtained by fusing from 150 to 200 g of the strongly acid crystals in a platinum crucible of about 80 cc capacity (4 cm maximum diameter by 4.5 cm high), keeping the temperature of the oven between 250° and 300° C and removing the salt as soon as melted.

During the fusion, as well as all other processes in the preparation of the salt, it should be protected from dust, etc., by means of a cover glass. That organic material is efficiently excluded in this way is shown by the fact that if mere traces are added to the salt before fusion their presence is readily revealed by the reducing properties of the fused salt toward thousandth normal permanganate solution.[20]

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[19] Since only a relatively small volume of air comes in contact with the salt under these conditions (especially since the vessel is covered with a watch glass during the fusion), the chance of contamination with dust is no greater than that arising from the necessary exposure of the water and solutions to the air in preparing the electrolyte and during electrolysis. The principal object of the air current in the work of Richards and Forbes seems to have been to aid in the complete expulsion of water and of nitric acid. Since the acid is expelled without this precaution and since water is not objectionable in the present instance, there is no necessity of employing a current of air in the present case.

[20] It should be stated at this point that the first samples of *fused* salt which conformed to the permanganate and iodeosine tests were prepared by Mr. F. E. Smith, of the National Physical Laboratory, in

The fusion may be made in platinum or transparent fused quartz vessels. Platinum vessels are very convenient for this purpose and are not attacked by the fused silver nitrate, provided the above conditions of temperature of fusion and acidity of the salt are observed. Otherwise the silver nitrate may be partially decomposed (reduced), and the platinum becomes stained with silver. If by accident this happens the stains can be removed with fused sodium bisulphate or by fusing a second portion of silver nitrate in the same dish, taking care to observe the proper precautions in fusing. The attack of fused *alkaline* nitrates upon platinum is usually attributed to the active oxygen given off by the nitrate, but the $KMnO_4$ test shows that under the conditions which we have described this does not occur. Salt fused in either platinum or quartz vessels leads to the same result.

1910. Deposits made from repeatedly crystallized, faintly acid crystals agreed well with the deposits from this fused salt, and, as stated before, we consider this agreement very important evidence of the high degree of purity of the fused salt. At this time the conditions which bring about a decomposition of the salt had not been fully worked out, and the conditions under which the fusion could be made without danger of decomposition had not been definitely specified. Also the above tests for reducing impurities and for neutrality had not previously been applied to any fused salt except to the preparations made in the very early part of our own work, to which reference has already been made, and in these cases the results seemed to show that the process of fusion was a rather hazardous procedure.

Smith prepared the fused salt referred to by fusing large quantities (between 500 and 1000 g) of the strongly acid crystals in a covered electric furnace until about half of the salt was melted and then turned off the heating current; the temperature of the oven was not taken.

Application of the permanganate and iodeosine tests to salt fused under varying conditions later made it possible to define the conditions which give best results, and when these are observed the salt practically always conforms to the criteria mentioned. Occasionally a fused sample has been obtained which did not prove satisfactory and yet which we supposed had been prepared under proper conditions. This emphasizes the importance of *always* applying the chemical tests before using the salt in the voltameter, and indicates further that some of the conditions, probably the rate of evaporation of the excess nitric acid, are somewhat difficult to control. In this connection it might be mentioned that some of the samples of fused salt referred to above which were prepared by Mr. F. E. Smith were found to be faintly basic (before use in the voltameter), and one in particular, which gave a higher value in the voltameter than usual, was 2 in 10^6 basic. Our later experience makes it seem very probable indeed that this basic reaction was due to a very slight decomposition of the salt during the fusion (as we suggested at the time) rather than to the action of the solution upon the glass, as suggested by Smith. The change in neutrality of dilute silver nitrate solution, due to glass cleaned with ordinary care, is very seldom greater than 1 part per million after standing for a month or longer. Constant agitation of course greatly increases the effect, and this, together with the fact that very soft glass was used, probably accounts for the instance cited by Smith in the International Report where an electrolyte originally 1.8 acid became about 0.3 basic after constant agitation in a flask. Ordinarily with resistant thoroughly cleansed Jena glass, such as was used to store the electrolyte referred to above, the effect of the glass has been found to amount to less than a part per million, even on standing for several weeks. On the other hand, the formation of base by overfusion has been noted even after the important factors that produce decomposition had been determined and when these were specially guarded against. Moreover, in some such cases the decomposition seemed not to have progressed far enough to produce an objectionable amount of reducing impurities (colloidal silver), as indicated by the permanganate test, but apparently had stopped at the formation of a slight amount of silver oxide, which, however, would increase the weight of the deposit.

III. SUMMARY

1. Using the small porous cup voltameter the value 1.01827_6 volts has been found for the Weston Normal Cell at 20° C.

2. The difference between the values obtained with the large porous cup voltameter and the smaller sizes is due to impurities present in the electrolyte, which may be partially removed by electrolysis. This phenomenon has been called the "volume effect."

3. The temperature coefficient of the voltameter appears to be zero if the electrolyte is pure.

4. Deposits on gold and platinum cathodes are in agreement.

5. For testing the purity of silver nitrate special methods have been devised. Estimations of the acidity may be made to 1 part in 1 000 000, using iodiosine as an indicator in the manner described. For testing the solutions for reducing agents and colloidal silver $\frac{N}{1000}$ potassium permanganate has been successfully used.

6. Methods of preparing silver nitrate of a satisfactory purity have been found. These differ considerably from previous methods owing to the conditions demanded by the voltameter work.

7. The fusion of silver nitrate has been discussed at length with particular reference to the decomposition of the salt after all of the acid has been expelled.

WASHINGTON, January 1, 1913.

NOTE ON COLD-JUNCTION CORRECTIONS FOR THERMOCOUPLES

By Paul D. Foote

Ordinarily, in the laboratory use of thermocouples, the cold junction is kept at a standard reference temperature such as the melting point of ice, while the hot junction is placed within the furnace or substance the temperature of which is desired. However, for technical purposes and general commercial use, it is not always convenient to have an ice box at hand. For this reason it is desirable to work with the cold junction at the temperature of the room. This necessitates a knowledge of the corrections to apply to the indicator readings, provided that the standardization of the pyrometer were carried out with the cold junction at some temperature other than that used in the technical works. The importance of these corrections is realized when one considers the large range of the cold-junction temperature which in practice frequently varies from 10 to 100° C.

In order to obtain the temperature corresponding to any value of the emf observed when the cold junction is at a temperature $t_0°$ C from the relation $e = f(t)$ computed on the basis that the cold junction is at $0° C$, it is only necessary to add to the observed emf the value of the emf developed when the cold junction is at $0° C$ and the hot junction is $t_0° C$, a number which is independent of the temperature of the furnace. However, many pyrometer galvanometers are calibrated to read temperature directly and have no scale of emf recorded. One must then express the correction in terms of degrees, and this quantity for any given value of the cold junction will depend, of course, upon the temperature of the hot junction for the reason that in general the relation between temperature and emf is not linear. A table, accordingly, might be prepared stating the corrections to be applied to the temperature observations for all values of the hot-junction temperature and all variations in the temperature of the cold junction.

The usual method of obtaining the cold-junction correction consists in multiplying the value of the cold-junction temperature by certain empirical factors. R. Vogel[1] computed these factors for a Heraeus (*Pt, 90Pt–10Rh*) couple having a cold junction of *50° C*. Offerhaus and Fischer[2] have calculated the factors for several types of couples.

This method of correction for cold-junction temperatures may be derived in the following manner:

Derivation of the Slope Correction.—Let e and t be the observed emf and corresponding temperature when the cold junction = $0°$ C.

e_1 and t_1 = the observed emf and temperature when the cold junction = $t_0°$ C.

For any thermocouple $\qquad e = f(t) \qquad (1)$

then for any value e_1 $\qquad e_1 = f(t_1) \qquad (2)$

But $\qquad e = e_1 + e_0$ where $e_0 = f(t_0)$ = emf developed when the hot junction = $t_0°$ and the cold junction = 0°C.

Substituting in (1) $\qquad e_1 + e_0 = f(t) \qquad (3)$

From (3) $\qquad t = \varphi\ (e_1 + e_0)$

From (2) $\qquad t_1 = \varphi\ (e_1)$

Denote by p the correction to add to the observed temperature when this value is read from the plot of a couple calibrated with its cold junction = $0°$ C.

$$p = t - t_1 = \varphi(e_1 + e_0) - \varphi(e_1)$$

$$= \varphi(e_1) + e_0\varphi'(e_1) + \frac{e_0^2}{\underline{|2}}\varphi''(e_1) + \ .\ .\ .\ - \varphi(e_1)$$

$= e_0\varphi'(e_1)$ provided e_0 and t_0 are small in comparison with e_1 and t_1

hence $\qquad p = \frac{e_0}{\varphi(e_0)}\varphi'(\mathrm{e}_1)\,\varphi(e_0) = \frac{e_0}{\varphi(e_0)} \cdot \frac{dt_1}{de_1} \cdot t_0$

$$= \frac{de_0}{dt_0}\ \frac{dt_1}{de_1}\ t_0 = \frac{\left(\frac{de}{dt}\right)_0}{\left(\frac{de}{dt}\right)_1}\ t_0 \qquad \text{approximately.}$$

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[1] R. Vogel: Zs. f. Anorg Chem., p. 45; 1905.

[2] Cornelis Offerhaus and E. H. Fischer: Electrochem. and Metal. Ind., Sept., p. 362–364; 1908.

This equation therefore states that in order to obtain the true temperature (t), it is necessary to add to the observed temperature (t_1), the quantity obtained by multiplying the temperature of the cold junction (t_o) by the ratio of the slopes of the calibration curve at the origin and at the temperature (t_1). The derivative $\left(\frac{de}{dt}\right)_o$ is but approximately equal to the quantity $\frac{e_o}{\varphi(e_o)}$ and becomes less so, the farther t_o departs from zero. As seen from Fig. 1, $\frac{e_o}{\varphi(e_o)}$ is more exactly the mean slope of the calibration curve from o to t_o° C. Using this value the single term slope correction becomes:

$$p=\frac{\left(\frac{de}{dt}\right)_{o-t_o}}{\left(\frac{de}{dt}\right)_1}\cdot t_o$$

The mean slope from o to t_o may be determined accurately enough by assuming some value of t_o in the neighborhood of the actual value of the cold-junction temperature such as 30° C, and computing the mean slope from o° to this point, i. e., the value of the emf observed when the cold junction is at o° and the hot junction 30° divided by 30. This form of the cold-junction correction requires but a single measurement of the emf at room temperature, whereas the usual form of correction practically necessitates a knowledge of the curve at several points in order to evaluate the slope at o° C. The three forms of the cold-junction temperature correction may be summarized thus:

Form I $\quad p=e_o\varphi'(e_1)+\frac{e_o^2}{\underline{|2}}\varphi''(e_1)+\ldots\ldots\frac{e_o^n}{\underline{|n}}\varphi^n(e_1)+\ldots$

Form II $\quad p=\frac{\left(\frac{de}{dt}\right)_o}{\left(\frac{de}{dt}\right)_1}t_o$

Form III $\quad p=\frac{\left(\frac{de}{dt}\right)_{o-30}}{\left(\frac{de}{dt}\right)_1}t_o$

Form I is the correct expression of the cold-junction correction.

Form II is the approximation in general use.

Form III is the approximation which should be given preference over Form II.

Magnitude of the Cold-Junction Correction.—Fig. 2 illustrates the magnitude of the true cold-junction corrections for P_8 a (Pt, $90Pt-10Rh$) Heraeus couple having for its temperature—emf relation the equations:

$e \times 10^4 = 56.04\ t + 0.05434t^2$ 0 to 100° C and

$e \times 10^4 = -2820 + 80.71t + 0.01694t^2$ 300 to 1500° C

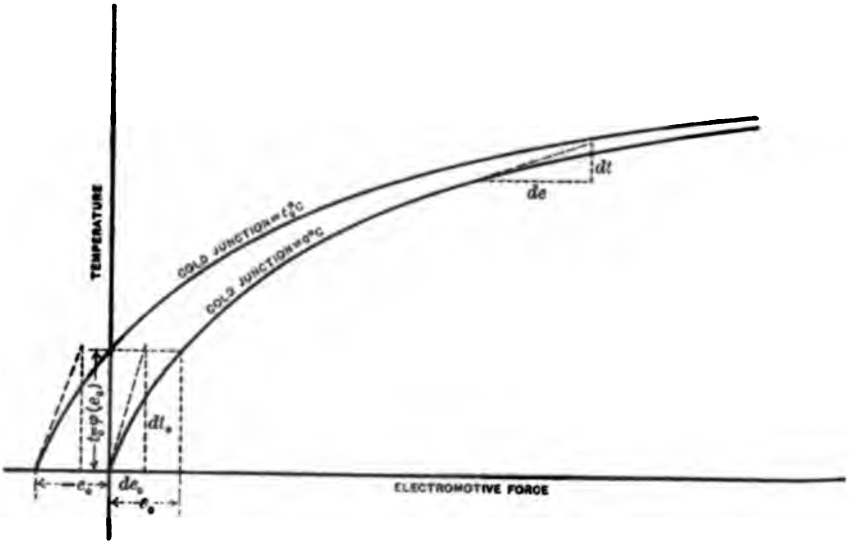

Fig. 1.—*Illustrating the shift of the thermocouple curve with a change of the cold-junction temperature*

where e is expressed in millivolts. These curves represent the *true* correction, Form I, for four observed hot-junction temperatures, and with the cold-junction temperature varying from 0 to 100° C. It is seen that the amount to be added to the observed temperature may reach a value as high as 60° or 65° C.

Errors in the Slope Corrections.—How closely Forms II and III express the true correction for the cold-junction temperature depends upon the form of the function $e=f\ (t)$. Inasmuch as the series in Form I is frequently only slowly convergent a more convenient method than evaluating each term was used for determining the errors in the approximation corrections.

Several of the Bureau of Standards' thermocouples were calibrated (cold junction = 0° C) from 0 to 1500° C. Assuming the temperature of the hot junction so regulated that any definite value of the observed emf developed by the couple remains constant whatever the temperature of the cold junction, the emf's for a cold junction 0° C were obtained by adding to the observed value, the emf readings between 0 and 100° C. The temperatures corresponding to these new emf's were computed and from them was subtracted the temperature corresponding to the observed emf. The differences are the true corrections to be applied to the observed temperature for a series of cold-junction temperatures. This operation was repeated for several different observed values of the emf. The slope corrections were then computed for the same points.

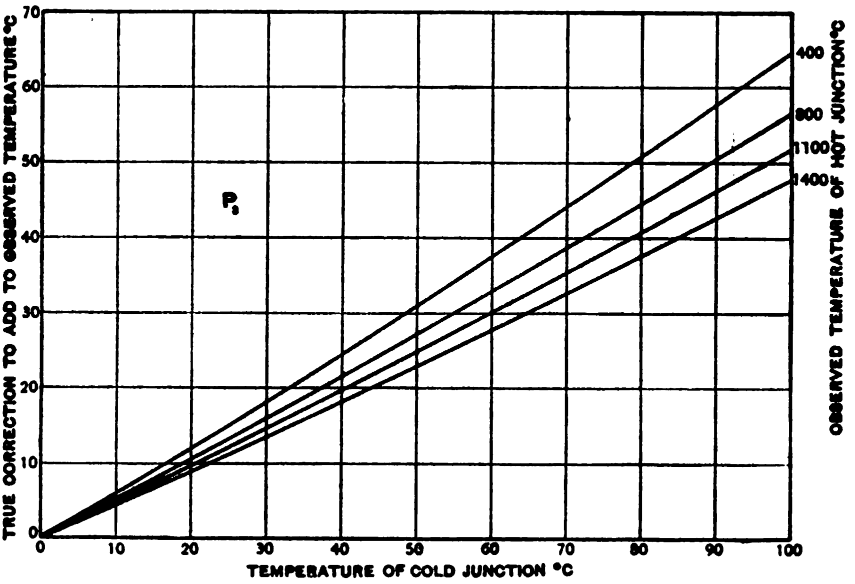

Fig. 2.—*True correction v. cold-junction temperature*

Fig. 3 presents the errors met with in the application of the slope corrections, Forms II and III, to P_s (Pt, $90Pt-10Rh$). The upper group of curves shows the amount to be added to the slope correction, Form II, to obtain the true correction. The largest error is 5°, with the hot junction at an observed temperature of 400° and the cold junction 100° C. The lower group of curves represents the corrections to apply when the slope correction is computed on the basis of the mean slope from 0 to 30° instead of 0° C, Form III. The errors are all somewhat smaller in this case, the maximum being 3°, and hence, in general, the correction according to Form III is to be preferred.

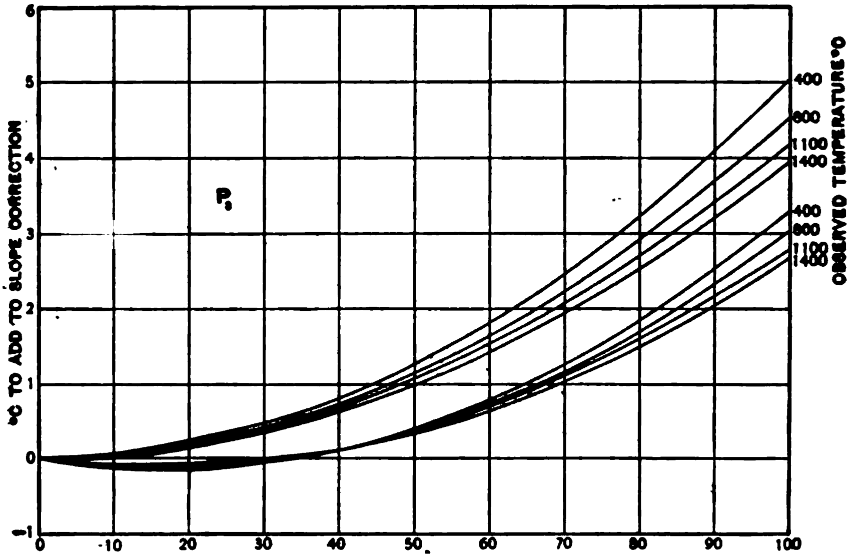

Fig. 3.—*Error in slope correction*

Similar curves were obtained for P_4, a Johnson and Matthey (Pt,90Pt–10Rh) couple having the equations:

$e \times 10^4 = 63.86t + 0.07343t^2$ 0 to 100° C

$e \times 10^4 = -4934 + 99.06t + 0.01594t^2$ 300 to 1,500° C

Fig. 4 illustrates the errors found in the use of the slope corrections with W_7. This couple which was obtained from Pellin, and supposed to have the composition (Pt,90Pt–10Ir), had a temperature-emf relation expressed by the equations:

$e \times 10^4 = 84.76t + 0.1603t^2$ 0 to 100° C

$e \times 10^4 = -6260 + 130.2t + 0.03381t^2$ 300 to 1,500° C

The maximum error found for Form II is about 9° with the hot junction at an apparent temperature of 400° and the cold junction 100° C. The lower group of curves is computed on the basis of the preferred form of the slope correction, Form III. The maximum error in this case is 6°.

For a copper-constantan couple of Adams and Johnston[8] having the equation:

e (microvolts) $= 38.105t + 0.04442t^2 - 0.00002856t^3$ applicable over a range 0 to 350° C, the ordinary slope correction, Form II, is in error from 0.1° to 0.5° when the cold junction varies from 0 to 20°. With a cold junction of 20 to 50° this slope correction is too small by amounts running from 0.5 to 2°. Form III applied to this couple shows corrections somewhat nearer those given by the true correction term, Form I.

Applicability of Slope Corrections.—If the couples examined are typical of all (Pt,90Pt − 10Rh), (Pt,90Pt − 10Ir), and copper-constantan couples, one may conclude that for values of the cold junction from 0 to 50° C in the case of the platinum-platinum alloy couples, and from 0 to 20° C in the case of the copper-constantan couple the slope correction, Form III, is fully applicable, and is not in error by amounts greater than the precision attainable with the ordinary pyrometric galvanometer. For all technical work, it is sufficient to add to the galvanometer temperature reading the number obtained by multiplying the ratio of the mean slope from 0 to t_0 and the slope at the observed temperature (t_1) by the temperature (t_0) of the cold junction.

The ratio of the slopes are given in the form of numerical factors for thermocouples tested at the Bureau of Standards, and to all technical purposes are alike for similar couples. Their determination requires only a rough temperature-emf calibration made independently of the pyrometer indicator. Instead of a table of figures, the observer need remember but two or three numbers applicable over all ranges of the cold-junction temperature. Thus in the use of P_2 with any type of galvanometer indicator, it is sufficient in ordinary pyrometric work to correct for the cold-junction temperature, t_0° C, by adding to the observed temperature,

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[8] L. H. Adams and J. Johnston; Am. J. Sci., **33**, p. 534, June, 1912.

t_1° C, the amount 0.6 t_0 from 400 to 700° C and 0.5 t_0 from 700 to 1400° C, where t_0 is less than 50. If closer accuracy is desired, a number of slope values computed to another significant figure, as given in Table 1, second column, or preferably the third column, must be used, and the corresponding corrections shown in Fig. 3 applied. For the highest attainable accuracy a potentiometer is required, and the emf corresponding to the temperature of the cold junction is added to the emf reading of the couple.

TABLE 1

Temperature Centigrade vs. Cold-Junction Factor

P_3 (Pt, 90Pt–10Rh)

Observed temperature	$\left(\frac{de}{dt}\right)\underset{0}{\div}\left(\frac{de}{dt}\right)_1$	$\left(\frac{de}{dt}\right)\underset{0-30}{\div}\left(\frac{de}{dt}\right)_1$	$\left(\frac{de}{dt}\right)\underset{30-40}{\div}\left(\frac{de}{dt}\right)_2$
°C			
400	0.59	0.61	0.63
500	.57	.59	.61
600	.55	.57	.59
700	.53	.55	.57
800	.52	.54	.56
900	.50	.52	.54
1000	.49	.50	.52
1100	.48	.48	.51
1200	.46	.47	.49
1300	.45	.46	.48
1400	.44	.45	.47

The second column shows the factor by which the value of the cold-junction temperature must be multiplied when using the old-type slope correction, Form II. The third column contains the factors computed from the preferred form of the slope correction, Form III. The fourth column shows the factors when the couple is calibrated with the cold junction at 30° C and used with a cold-junction temperature not far from 40° C.

Slope Correction when the Couple is Calibrated with the Cold Junction at a Temperature other than 0° C.—Many thermocouple pyrometers are so constructed that it is impracticable to calibrate them with a cold junction at 0° C. Suppose the standardization were carried out with a cold junction of ${}_1t_0 = 30$° C and it is desired to use the couple near a furnace where the room temperature is ${}_2t_0 = 40$° C. Proceeding by a method similar to that shown in the derivation of the ordinary slope correction, we now obtain the correction term:

$$p = \frac{e_0}{{}_2t_0 - {}_1t_0}\,\varphi'(e_2)\;({}_2t_0 - {}_1t_0)$$

where $\varphi'(e_2)$ is the slope at the point corresponding to the observed emf, and $e_0 =$ the emf developed when the cold junction is at the temperature $_1t_0$ and the hot junction $_2t_0$, or—

$$p = \frac{\left(\frac{de}{dt}\right)_{30-40}}{\left(\frac{de}{dt}\right)_2} ({}_2t_0 - 30)$$

where $_2t_0$ is not far from 40, t_2 being the observed temperature corresponding to e_2. This equation, therefore, states that in order to obtain the true temperature, t, it is necessary to add to the observed temperature, t_2, the quantity obtained by multiplying the difference in the temperature of the cold junction used in the standardization, $_1t_0 = 30$, and during any observation, $_2t_0 = 40$, by the ratio of the mean slope of the calibration curve from 30 to 40° and the slope at the observed temperature. The mean slope from 30 to 40° is obtained by dividing the emf observed when the cold junction is 30° and the hot junction is 40° by 10. The factors for P_2 used in this manner are given in Table 1, column 4.

Reduction to Fahrenheit Scale.—All the temperatures referred to above are given in degrees centigrade. The conversion to the Fahrenheit scale occasions no difficulty. When the couple is originally calibrated with the cold junction at the temperature of melting ice, 32° F, and used with the cold junction at the temperature t°_0 F, the actual temperature, t, of the hot junction is obtained by adding to the observed temperature, t_1, the value of the product $(t_0 - 32)K$, instead of $t \cdot K$, where K is the correction factor at the particular observed hot-junction temperature. If the couple is calibrated with the cold-junction temperature of $_1t^\circ_0$ F and used with the cold junction at a temperature $_2t^\circ_0$ F., the correction term to be added to the observed temperature t_2 has the same form as before—

$$p = ({}_2t_0 - {}_1t_0)K'$$

where K' is the factor computed from the mean slope between $_1t_0$ and $_2t_0$ and the slope at the observed temperature. The values of the ordinates for the curves in Figs. 2, 3, and 4 should be increased by the factor 9/5, while the abscissas are directly converted to the Fahrenheit scale. As an example, in the case of Fig. 4 the ordinates will lie between the 0 and 18, the abscissas between 32 and 212° F and the observed temperatures of the hot junction become 752, 1472, 2012, and 2552° F. In Table 2 are given the correction factors for P_8 (*Pt*, 90*Pt* – 10*Rh*) for a series of observed temperatures °F. These follow directly from Table 1. The second column shows the factors computed on the basis of the old-slope correction, Form II. The third column contains the factors computed from the preferred slope correction, Form III. In the fourth column are given the correction factors when the couple is calibrated with a cold-junction temperature of 86° F and used with the cold junction not far from 104° F.

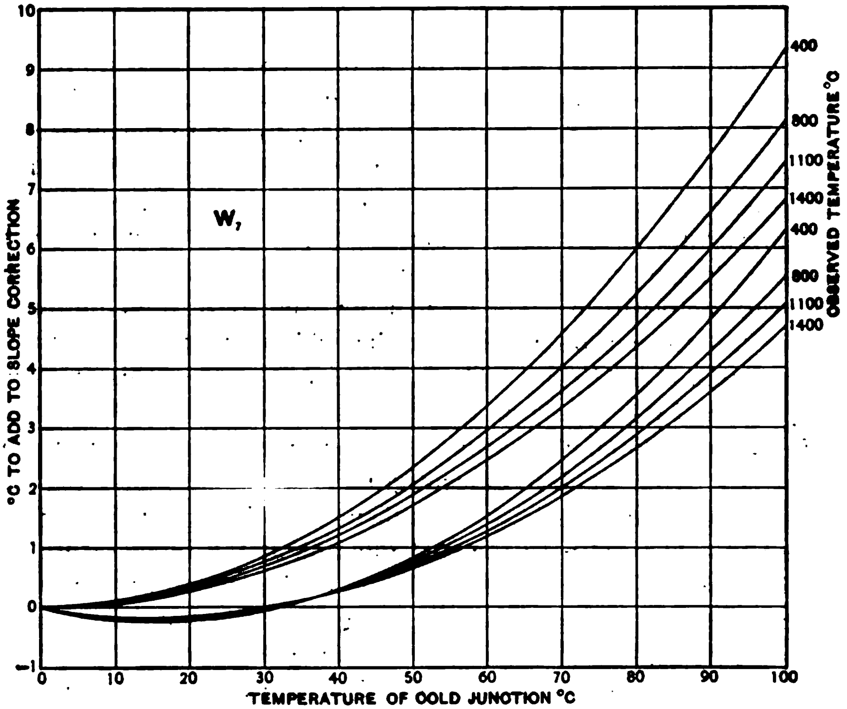

Fig. 4.—*Error in slope correction*

TABLE 2

Temperature Fahrenheit v. Cold-Junction Factor

P_3 (Pt, 90 Pt—10 Rh)

Observed temperature.	$\left(\frac{de}{dt}\right)_{32} \div \left(\frac{de}{dt}\right)_1$	$\left(\frac{de}{dt}\right)_{32\text{-}86} \div \left(\frac{de}{dt}\right)_1 - K$	$\left(\frac{de}{dt}\right)_{86\text{-}104} \div \left(\frac{de}{dt}\right)_2 - K'$
°F.			
800	0.59	0.61	0.63
1000	.56	.58	.60
1200	.54	.56	.58
1400	.53	.54	.56
1600	.51	.52	.54
1800	.49	.51	.53
2000	.48	.49	.51
2200	.46	.47	.49
2400	.44	.45	.48
2600	.43	.44	.46

Conversion of the Thermoelectric Scale to the Standard Temperature Scale.—When the ordinary parabolic equation $e = a + bt + ct^2$ is applied to a (*Pt*, 90 *Pt*—10 *Rh*) or (*Pt*, 90 *Pt*—10 *Ir*) thermocouple standardized at three temperatures, the melts of zinc, antimony, and copper, the curve extrapolated to 1500° C differs somewhat from the temperature shown by the gas thermometer. This is treated in full in The Measurement of High Temperatures, pages 112–116 loc. cit., but may be briefly summarized in the following table, which holds approximately for the usual type of platinum, platinum-iridium and platinum-rhodium couples.

TABLE 3

Correction to Thermocouple Scale

Thermocouple scale.	Correction to add degrees Centigrade.	Thermocouple scale.	Correction to add degrees Fahrenheit
°C.		°F.	
300-1200	0	600-2200	0
1300	+ 2	2400	+ 5
1400	+ 6	2600	+14
1500	+14	2800	+35

The above discussion of couples P_8, P_4, and W_7 is on the basis of the thermoelectric scale. Hence, temperatures higher than 1200° C or 2200° F should be further corrected in accordance with Table 3. The order of applying the cold-junction correction and the above correction is of little importance, since both are small. Couples calibrated by the Bureau of Standards are corrected as shown in Table 3, so that the temperatures indicated by them accord with the established gas thermometer scale.

Devices for the Elimination of the Cold-Junction Corrections.—Various methods have been proposed for the elimination of the cold-junction corrections. If a coil of copper wire were shunted across the terminals of the thermocouple in the head of the instrument, an increase in the temperature of the cold junction, ordinarily producing a decrease in the observed emf would increase the resistance of the shunt and thus tend to compensate for the thermoelectric effect. However, for exact compensation at all temperature ranges, a coil of wire would be required of which the resistance is a function not only of its own temperature, but also of the hot-junction temperature. This, of course, is impossible to realize in practice, but the method might be applied as a partial correction.

Bristol[4] base metal couples are provided with extension wires which permit the location of the cold junction in a constant temperature room some distance from the furnace. Bristol has also devised an automatic compensator consisting of a bulb of mercury into which a loop of platinum wire dips. This is inserted in the circuit near the head of the couple so that the variations in the cold-junction temperature cause the mercury to expand or contract and short-circuit different lengths of the wire loop, thus altering the resistance with a result somewhat similar to that obtained by the use of a shunt coil.

Hartmann and Braun have the cold-junction head jacketed in order that a stream of water may be used to keep the head at a uniform temperature.

The Crompton Co. use a multiple scale on their galvonometers so constructed that the pointer reads directly the temperature of the furnace, each scale corresponding to some definite value of the cold-junction temperature.

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[4] The following and other methods of cold-junction compensation are discussed in The Measurement of High Temperatures, Burgess and Le Chatelier, p. 156, 3d ed., 1912, Wiley, New York.

Several instrument makers have tried interposing a supplementary thermocouple circuit of inexpensive material, the hot junction being located at the cold end of the main thermocouple and the cold junction at the galvanometer, some distance away.

Possibly the most simple compensating device is that employed by Siemens and Halske, and one or two other firms. Here the galvanometer indicator has a large zero adjustment so constructed that the pointer may be set, on open circuit, at the temperature corresponding to that of the cold junction, the graduations having been previously empirically determined for the given thermocouple.

All of these methods possess certain advantages but many of them are open to the objection that they are cumbersome and frequently liable to introduce new errors. Attention might well be given to the more careful construction of the indicating instruments. Many galvanometers have a temperature coefficient so large that small variations in the room temperature affect the readings to a marked degree. This may give rise to errors as large as those commonly found for the cold-junction temperature.

It is moreover needless to mention that the ordinary indicator should not be used in close proximity to other magnetic instruments or to iron unless originally calibrated in that position. A simple trial will readily convince one that this precaution is necessary.

When due care is exercised to locate the galvanometer in such a position that its magnetic field is not disturbed by outside influences and where its temperature is reasonably constant, to occasionally recheck the thermocouple calibration, and to properly correct for the cold-junction temperatures, the simple thermocouple without any compensating devices whatever will prove very satisfactory.

Acknowledgement is due Mr. I. N. Kellberg for computing and drawing the curves shown, and to Dr. G. K. Burgess for a number of suggestions.

WASHINGTON, April 15, 1913.

ANALYSIS OF ALTERNATING-CURRENT WAVES BY THE METHOD OF FOURIER, WITH SPECIAL REFERENCE TO METHODS OF FACILITATING THE COMPUTATIONS

By Frederick W. Grover

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I. INTRODUCTION.

The value of curves, showing the wave form of the electromotive force and the current in a circuit, has long been recognized, not only in the study of alternating-current phenomena, but also in precise electrical measurements, and in the design of alternating-current machinery, and various instruments have been designed for drawing such curves. These may naturally be divided into two classes—curve tracers and oscillographs. Of these, the first type is capable of giving the more precise results. The use of a curve tracer, however, presupposes steady conditions, so that the successive cycles of the wave are sensibly exact repetitions of those which have preceded. For transient phenomena the oscillograph is more suitable, and has in recent years become a powerful instrument of research. For a comprehensive and up-to-date treatment of the history and development of curve-drawing instruments, the reader is referred to the valuable treatise, "Aufnahme und Analyse von Wechselstromkurven," by E. Orlich, F. Vieweg und Sohn, Braunschweig, 1909.

Having obtained the desired curves, a simple inspection is in some cases perhaps sufficient to throw light on the problem under consideration. More often, however, and especially where quantitative results are desired, it is necessary to make an analysis of the curve in order to realize its full value. To make such analyses, various ingenious and elaborate machines, the so-called "harmonic analyzers," have been devised, which automatically carry out the resolution of a given irregular curve into a number of component sine waves, the number depending on the number of elements included in the machine. Where a great many curves have to be analyzed, such instruments can hardly be dispensed with. Usually, however, the number of curves which have to be analyzed will hardly warrant the expense of such a machine, and one has recourse to calculation for obtaining the component waves.

The logical procedure in this case would seem to be to make use of the method of Fourier, who in his classic work on the theory of heat gave the complete solution of the problem of the resolution of a given function into a series of component sine terms. The direct use of the Fourier equations involves, however, the necessity of the formation of so many products, that the calculation is very laborious, and it is to this fact that the neglect of the Fourier method for numerical calculations is to be attributed. To avoid the difficulty, recourse has been had in a great many cases to graphical or approximate mathematical solutions, or the curve has been put aside without any analysis at all.

Realizing the greater accuracy of the Fourier method, attempts have been made from time to time to reduce the amount of labor involved in the use of Fourier's equations. Thus Perry[1] and Kintner[2] sought to simplify the calculation by the preparation of printed blank forms, in which were indicated the products to be taken in their proper places for making the summations.

A further step was taken by Rosa, who in 1897 worked out the details of a scheme of calculation, in which from 15 measured ordinates, equally spaced throughout a half wave, all odd harmonics up to and including the fifteenth can be obtained. From a consideration of the relations between the sines and cosines of supplementary and complementary angles it is easy to show that, for this case, the only functions involved are the sines of 6°, 12°, 18°, ... 90°. To facilitate the multiplication of the ordinates by these sines, Rosa prepared a multiplication table with 14 columns, in which were tabulated the calculated products of the sines of the 14 angles, other than 90°, by values of ordinates up to 50 by steps of 0.1. The calculation of the harmonics was arranged according to a definite form, each product being indicated by the number of that column, in the table, which must be entered with the values of ordinate in question.

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[1] Lond. Elect. Feb. 5, 1892, and June 28, 1895.

[2] Elect. World, **43**, p. 1023; 1904.

The number of required products, when this scheme of analysis is used, is, omitting those involving sin 30° and sin 90°, 160 in number. The products omitted in this count do not of course add materially to the labor. With very little practice one can carry through a complete analysis in about 45 minutes, and this time could be reduced materially by the use of printed forms, to save the time required for writing down the numbers of the columns and the headings. This scheme, which has never been published, has been used with success for analyzing a large number of curves taken with the Rosa curve tracer; a special application was its employment for determining the correction for wave form in absolute measurements of inductance made at the Bureau of Standards.[3]

An extension of this principle of simplification of the calculation by grouping terms was carried out by Runge[4] in 1903. This method, which is described in detail below, consists in separating those products which involve the same trigonometrical function. By previously adding together the ordinates which enter into these products, the sum of the products in question is obtained with the necessity of making a single multiplication only. The paper of Runge treats the problem in an entirely general manner, and without reference to any specific problem, the number of harmonics being unrestricted. He works out in detail the scheme of calculation for the cases of 18 and 36 ordinates.

The paper of Runge does not seem to have received the attention it deserves. In 1905 S. P. Thompson[5] reviewed Runge's article, and worked out schedules for the analysis of curves from 6 and 12 measured ordinates, only odd harmonics being assumed present. The author of the present paper, after reading the article of Thompson in 1909, extended the use of the method to the case of 18 ordinates with only odd harmonics present. These three schedules are given below together with the corresponding schemes of calculation when even harmonics are present. Of the latter, that for 12 points was given by Runge; the other two have been derived by the author. During the writing of the present paper, has appeared an excellent though necessarily brief treatment of the subject of wave analysis by the method of Runge in an appendix to the "Direct and alternating current manual" of Bedell and Pierce, second edition, 1911.

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[3] Rosa and Grover, This Bulletin, 1, p. 138; 1904.

[4] Zs. für Math. und Phys., 48, p. 443; 1903.

[5] Lond. Elect., 55, p. 78; May 5, 1905.

Nevertheless, knowledge of the work of Runge seems to be far from general, and the Fourier analysis of alternating-current curves seems to be a thing avoided by the majority of electrical engineers. To such considerations this paper owes its origin. In it the author has endeavored to include all the necessary formulas, together with a detailed description of the methods of carrying out the calculations and checking their correctness. As a further aid toward clearness all the formulas and schemes of calculation have been illustrated by means of examples of the analyses of actual curves. A useful feature will, it is believed, be found in the multiplication tables, which allow all necessary products to be found without calculation.

For the sake of completeness, the first part of the paper includes a proof of the equations of Fourier, for the case of a finite number of terms, and with even harmonics absent. This proof follows closely the method of treatment given in Byerly's "Fourier's series and spherical harmonics."

The latter part of the paper is taken up with the consideration of some of the practical applications of curve analysis in the realm of alternating-current theory. These may perhaps appeal most strongly to the teacher, but it is hoped that they may be of use, in any case, as illustrations of general methods of attack for special problems.

Although alternating-current waves are the only cases treated here, it hardly needs to be pointed out that the methods and results here given may, with little change, be applied to the treatment of periodic curves relating to other branches of science. This will be especially true of the analysis schedules for curves in which even harmonics are present.

The electromotive force and current waves reproduced here were all taken from originals drawn by means of the Rosa curve tracer.[6] For details of this instrument the reader is referred to the original article. Briefly, the instrument operates on a point-by-point method, the instantaneous fall of potential over a resistance, through which an alternating current is flowing being applied by means of a rotating contact maker to a potentiometer arrangement, the instantaneous emf being balanced by varying the position of a movable contact (on the potentiometer), which position can be automatically registered. The curves themselves bear witness to the faithfulness with which even insignificant irregularities of the wave may be recorded.

Finally, I wish to express my indebtedness to Prof. Rosa for the wealth of curves which he has placed at my disposal, but especially for my first interest in the subject and the advantage of an intimate knowledge of his work along this line.

II. THE FOURIER METHOD

1. DERIVATION OF FOURIER'S EQUATIONS FOR A FINITE NUMBER OF TERMS

By the method of Fourier any function may, between definite limits, be expressed as a series of sine and cosine terms in the form

$$\begin{aligned} y=f(x)=A_1\sin x+A_2\sin 2x+A_3\sin 3x \\ +\ \ldots\ +A_n\sin nx+\ \ldots \\ +B_0+B_1\cos x+B_2\cos 2x+B_3\cos 3x \\ +\ \ldots\ +B_n\cos nx+\ \ldots \end{aligned} \qquad (1)$$

where $A_1, A_2, \ldots\ldots A_n, B_0, B_1, B_2, \ldots\ldots B_n$ are constants. To obtain any coefficient A_k, for example, Fourier multiplied both sides of the equation (1) by $\sin kx\,dx$ and integrated between the limits zero and X, where X is the interval through which it is desired that the development shall hold. Since all the integrals of the forms $\int_0^X A_m \sin mx \sin kx dx$ and $\int_0^X B_m \cos mx \sin kx dx$ become severally equal to zero, the resulting equation is simply

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[6] Phys. Rev., 6, p. 17; 1898.

$$\int_0^X y \sin kx dx = \int_0^X A_k \sin^2 kx dx$$

or

$$A_k = \frac{2}{X}\int_0^X y \sin kx dx$$

Similarly, the general coefficient B_k of the cosine terms is found by multiplying both members of (1) by $\cos kx dx$ and by integrating between zero and X, and we find finally,

$$B_k = \frac{2}{X}\int_0^X y \cos kx dx$$

These, which are known as the Fourier integrals, can not, in general, be evaluated, since the relation connecting y and x is usually unknown or too complicated.

The series (1) is an infinite series; only when the number of terms is infinitely great will the function be represented by the series for every value of x in the chosen interval. If n have a finite value, the series (1) will be a finite series, and the series will be equal to the function at only n points, the deviation between the function and the series being smaller the greater n is taken. Fortunately in the case of alternating current waves, the number of terms required in order that the deviations between the curve and the series may be negligible is seldom very large. Further, from the fact that well-designed alternators give waves of which the positive and negative loops are closely of the same form, it is only necessary to include terms involving the sines and cosines of odd multiples of x.

An alternating current wave may therefore in general be represented by the equation

$$\begin{aligned} y = {} & A_1 \sin pt + A_3 \sin 3pt + A_5 \sin 5pt + \ldots \\ & + A_k \sin kpt + \ldots \quad + A_{2n-1} \sin (2n-1)pt \\ & + B_1 \cos pt + B_3 \cos 3pt + B_5 \cos 5pt + \ldots \\ & + B_k \cos kpt + \ldots \quad + B_{2n-1} \cos (2n-1)pt \end{aligned} \tag{2}$$

where $p = 2\pi$ times the frequency.

If, therefore, ordinates of the wave be measured at $2n$ equally spaced points in the half wave, a set of $2n$ simultaneous equations of the form

$$\begin{aligned} y_0 = {} & B_1 + B_3 + B_5 + \ldots \quad + B_k + \quad \ldots \quad + B_{2n-1} \\ y_1 = {} & A_1 \sin \frac{\pi}{2n} + A_3 \sin \frac{3\pi}{2n} + \ldots \quad + A_k \sin \frac{k\pi}{2n} + \ldots \\ & + A_{2n-1} \sin \frac{(2n-1)\pi}{2n} + B_1 \cos \frac{\pi}{2n} + B_3 \cos \frac{3\pi}{2n} + \ldots \\ & + B_k \cos \frac{k\pi}{2n} + \ldots + B_{2n-1} \cos \frac{(2n-1)\pi}{2n} \ldots \\ y_m = {} & A_1 \sin \frac{m\pi}{2n} + A_3 \sin \frac{3m\pi}{2n} + \ldots + A_k \sin \frac{mk\pi}{2n} + \ldots \\ & + A_{2n-1} \sin \frac{m(2n-1)\pi}{2n} + B_1 \cos \frac{m\pi}{2n} + B_3 \cos \frac{3m\pi}{2n} \\ & + \ldots + B_k \cos \frac{mk\pi}{2n} + \ldots + B_{2n-1} \cos \frac{m(2n-1)\pi}{2n} \\ y_{2n-1} = {} & A_1 \sin \frac{(2n-1)\pi}{2n} + A_3 \sin \frac{3(2n-1)\pi}{2n} + \ldots \\ & + A_k \sin \frac{k(2n-1)\pi}{2n} + \ldots + A_{2n-1} \sin \frac{(2n-1)^2\pi}{2n} \\ & + B_1 \cos \frac{(2n-1)\pi}{2n} + B_3 \cos \frac{3(2n-1)\pi}{2n} + \ldots \\ & + B_k \cos \frac{k(2n-1)\pi}{2n} + \ldots + B_{2n-1} \cos \frac{(2n-1)^2\pi}{2n} \end{aligned} \tag{3}$$

will be obtained, which are sufficient to determine the $2n$ unknown coefficients in equation (2), and the analysis will take into account all the odd harmonics up to and including that of order $(2n-1)$. The curve represented by the equation (2) will intersect the actual curve at those points whose measured ordinates enter into equation (3) and the magnitude of the deviations between the curve and series at the other points will give an idea as to the importance of those harmonics not taken into account by the analysis.

To obtain the value of the general coefficient A_k of the sine terms in (3), multiply both sides of the equation for y_1 by $2 \sin \frac{k\pi}{2n}$, the equation for y_2 by $2 \sin \frac{2k\pi}{2n}$, etc., and add the resulting equations. The first member of the sum becomes $2\Sigma_{m=1}^{m=2n-1} y_m \sin \frac{mk\pi}{2n}$.

In the second member the general coefficient A_r (where r can have any value except k) is multiplied by the factor

$$2\Sigma_{m=1}^{m=2n-1} \sin \frac{mr\pi}{2n} \sin \frac{mk\pi}{2n} = 2\Sigma_{m=1}^{m=2n-1} \left[\cos \frac{m(r-k)\pi}{2n} - \cos \frac{m(r+k)\pi}{2n} \right]$$

Making use of the lemma[7]

$$\cos x + \cos 2x + \cos 3x + \dots$$
$$+ \cos(s-1)x + \cos sx = -\tfrac{1}{2} + \tfrac{1}{2} \frac{\sin(2s+1)\frac{x}{2}}{\sin \frac{x}{2}} \tag{4}$$

and remembering that $(r-k)$ and $(r+k)$ are even integers, it is easy to show that the factor by which A_r is multiplied is equal to zero.

The coefficient B_r (where r may have any value, not excluding k) is

$$2\Sigma_{m=1}^{m=2n-1} \sin \frac{mr\pi}{2n} \cos \frac{mk\pi}{2n} = 2\Sigma_{m=1}^{m=2n-1} \left[\sin \frac{m(r-k)\pi}{2n} + \sin \frac{m(r+k)\pi}{2n} \right]$$

and making use of the lemma[7]

$$\sin x + \sin 2x + \sin 3x + \dots$$
$$+ \sin(s-1)x + \sin sx = \tfrac{1}{2} \frac{\sin \frac{sx}{2} \sin(s+1)\frac{x}{2}}{\sin \frac{x}{2}} \tag{5}$$

the factor by which B_r is multiplied is also seen to be equal to zero.

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[7] Byerly's Fourier's Series and Spherical Harmonics, p. 32.

There consequently remains in the second member only one term

$$2A_k\Sigma_{m=1}^{m=2n-1} \sin \frac{2mk\pi}{2n} - A_k\left[(2n-1) - \Sigma_{m=1}^{m=2n-1} \cos \frac{mk\pi}{n}\right]$$

which by (4) reduces to $2nA_k$, and we have finally

$$2nA_k = 2\Sigma_{m=1}^{m=2n-1} y_m \sin \frac{mk\pi}{2n}$$

or (6)

$$A_k = \frac{1}{n}\Sigma_{m=1}^{m=2n-1} y_m \sin \frac{mk\pi}{2n}$$

To obtain B_k we multiply both sides of the equation for y_0 by 2, the equation for y_1 by $2 \cos \frac{k\pi}{2n}$, the equation for y_2 by $2 \cos \frac{2k\pi}{2n}$, etc., and add these equations. The first member of the resulting equation is $2\Sigma_{m=0}^{m=2n-1} y_m \cos \frac{mk\pi}{2n}$.

In the second member, the coefficient of A_r is

$$2\,\Sigma_{m=1}^{m=2n-1} \sin \frac{mr\pi}{2n} \cos \frac{mk\pi}{2n},$$

which we have already shown reduces to zero.

The general coefficient B_r, where r does not have the value k, is affected by the factor

$$2\Sigma_{m=0}^{m=2n-1} \cos \frac{mk\pi}{2n} \cos \frac{mr\pi}{2n}$$
$$= 2 + \Sigma_{m=1}^{m=2n-1}\left[\cos \frac{m(r+k)\pi}{2n} + \cos \frac{m(r-k)\pi}{2n}\right]$$

which by use of the lemma (4) can be shown to be equal to zero.

There remains therefore in the second member, one term only, $2B_k\Sigma_{m=0}^{m=2n-1} \cos^2 \frac{mk\pi}{2n} = 2nB_k$ and the value of B_k follows at once.

It has been shown, therefore, that the alternating wave can be represented by the finite series (2) at $2n$ points of the half wave, and that the coefficients in (2) are capable of calculation from the $2n$ ordinates of these points, by the simple relations

$$A_k = \frac{1}{n}\Sigma_{m=0}^{m=2n-1} y_m \sin \frac{mk\pi}{2n}, \quad B_k = \frac{1}{n}\Sigma_{m=0}^{m=2n-1} y_m \cos \frac{mk\pi}{2n} \qquad (7)$$

The coefficients of the sine terms in (2) are therefore found by taking the averages of the measured ordinates of the curve, each ordinate having been multiplied by the sine of an appropriate multiple of that angle which indicates the position of the ordinate in question. Similarly, the coefficients B_k of the cosine terms are found by averaging the products of the measured ordinates y_m and the cosines of the same multiples of the abscissas. For example, if 12 ordinates are measured with abscissas equally spaced 15° apart, to find the coefficient B_3 we are directed by equation (7) to multiply y_0 by $\cos 0°$, y_1, by $\cos 3 \times 15°$, y_2 by $\cos 2 \times 3 \times 15°$, etc., to add these 12 products, and to divide the sum by 6.

Simple as are the operations indicated in (7) for finding the coefficients in the Fourier's series development for an alternating current wave, it is, however, evident that the amount of labor involved in evaluating the coefficients must increase rapidly with the number of harmonics taken into account; that is, with the number of terms included in the series. If any considerable number of harmonics are to be found, it will become necessary to systematize the calculation in order to avoid confusion and to guard against error.

2. RUNGE'S METHOD OF GROUPING

Of the methods which have been suggested, the one which best serves the purpose is that of Runge; it is used in the methods of analysis considered below.

We note, first, that it it is an advantage to use an even number of measured ordinates per half wave, rather than an odd number. Not only is the necessity avoided for the calculation of one of the coefficients from an extra set of ordinates, as remarked above in the case of A_{15}, but it has the further advantage that the grouping of terms involving the sines of common angles can be further extended, and the calculation of certain higher harmonics can be made to depend in a simple manner on the calculation of the lower harmonics.

In general, since k is an odd number

$$\begin{aligned} \sin\frac{mk\pi}{2n} &= \sin\,(2n-m)\frac{k\pi}{2n}, & \cos\frac{mk\pi}{2n} &= -\cos\,(2n-m)\frac{k\pi}{2n} \\ \sin k\frac{m\pi}{2n} &= \pm\sin\,(2n-k)\frac{m\pi}{2n}, & \cos k\frac{m\pi}{2n} &= \mp\cos\,(2n-k)\frac{m\pi}{2n} \end{aligned} \qquad (8)$$

In those cases where the double sign appears, the upper sign holds for odd values of m and the lower sign for even values of m.

The first two of the equations (8) show that in the fundamental equations (7) the measured ordinates y_m and y_{2n-m} are to be multiplied by the sine of the same angle, and, excepting for the algebraic sign, by the same cosine. Therefore, by adding y_m and y_{2n-m} before multiplying by the sine, and by taking the difference of y_m and y_{2n-m} before multiplying by the cosine, the number of products to be obtained is halved. In this method, therefore, we obtain at the start the quantities $s_m = y_m + y_{2n-m}$ and $d_m = y_m - y_{2n-m}$, the sums and differences of complementary ordinates.

From the last two equations of (8) it is evident that the products entering into the calculation of the coefficients A_k and B_k, on which the amplitude of the kth harmonic depends, are also required in the calculation of the $(2n-k)$th harmonic. It is not difficult to show that if we separate those products which involve even ordinates from those involving the odd ordinates, and take the respective sums S_e and S_o of the sine products involving the s_{2m} and s_{2m+1} and the sums D_e and D_o of the products involving the d_{2m} and d_{2m+1}, respectively, then the coefficients A_k, A_{2n-k}, B_k, B_{2n-k} are given by the following relations:

$$\begin{aligned} A_k &= S_o + S_e, \qquad & A_{2n-k} &= S_o - S_e \\ B_k &= D_o + D_e, \qquad & B_{2n-k} &= D_o - D_e \end{aligned} \tag{9}$$

The coefficients may consequently be separated into two complementary groups. For those harmonics whose order k is a factor of $2n$, the calculation becomes yet simpler. Putting $\frac{k}{2n} = \frac{1}{\nu}$, where ν is an integer, we have

$$\sin\frac{mk\pi}{2n} = \sin\frac{m\pi}{\nu} = -\sin\frac{m+\nu}{\nu}\pi = \sin\frac{m+2\nu}{\nu}\pi,$$

$$\cos\frac{mk\pi}{2n} = \cos\frac{m\pi}{\nu} = -\cos\frac{m+\nu}{\nu}\pi = \cos\frac{m+2\nu}{\nu}\pi, \text{ etc.,}$$

and if, further, m is exactly divisible by ν, $\sin \frac{mk\pi}{2n} = \pm 1$, $\cos \frac{mk\pi}{2n} = \text{zero}$, and for values of m half as great, $\sin \frac{mk\pi}{2n} = \pm 1$, $\cos \frac{mk\pi}{2n} = \text{zero}$. A considerable number of terms, therefore, involve the factor zero or unity, or at least the sine or cosine of the same angle.

III. SCHEDULES FOR CARRYING OUT ANALYSES

1. ARRANGEMENT OF CALCULATIONS

From these considerations are derived the following schedules based, respectively, upon systems of 6, 12, or 18 equally spaced measured ordinates. Blank forms can easily be prepared, to save clerical labor, if many calculations have to be made.

TABLE 1

Six Point Schedule

Measured ordinates	Sums	Diffs.		Sine terms			Cosine terms		
				1st and 5th		3d	1st and 5th		3d
y_0		d_0							
y_1 y_5	s_1	d_1	sin 30°	s_1			d_2		
y_2 y_4	s_2	d_2	" 60°		s_2			d_1	
y_3	s_3		" 90°	s_3		s_1-s_3	d_0		d_0-d_2
			sums	S_e	S_o	S	D_e	D_o	D
				$A_1=\frac{S_e+S_o}{3}$		$A_3=\frac{S}{3}$	$B_1=\frac{D_e+D_o}{3}$		$B_3=\frac{D}{3}$
				$A_5=\frac{S_e-S_o}{3}$			$B_5=\frac{D_e-D_o}{3}$		

In each of these schedules the measured ordinates are first written down in two columns in the order indicated. In the next two columns appear the sums s_m of the ordinates, found by adding those in the same row, and the differences d_m of the same ordinates. In the fifth column are indicated the trigonometric functions which enter into the calculation. The rest of the schedule indicates in an abbreviated form what products are to be formed, the convention being adopted that each quantity s_m or d_m is to be be multiplied by the sine of the angle which appears in the same row at the left. For example, in the 6-point schedule, we are to take the product of s_1 and sin 30° in one case, and in another the product of d_2 and sin 30°. It is also to be noticed that each product which is involved in the calculation of any coefficient, stands in the left or right-hand column, according as it depends upon odd or even ordinates. For example, in the calculation of the fifth and seventh harmonics in the 12-point schedule, we have to form the products s_5 sin 15°, $-s_3$ sin 45°, and s_1 sin 75° and take

TABLE 2

Twelve Point Schedule

Measured ordinates	Sums	Diffs.		Sine terms					
				1st and 11th		3d and 9th		5th and 7th	
y_0		d_0							
y_1 y_{11}	s_1	d_1	sin 15°	s_1				s_5	
y_2 y_{10}	s_2	d_2	" 30°		s_2				s_2
y_3 y_9	s_3	d_3	" 45°	s_3		σ_1		$-s_3$	
y_4 y_8	s_4	d_4	" 60°		s_4				$-s_4$
y_5 y_7	s_5	d_5	" 75°	s_5				s_1	
y_6	s_6		" 90°		s_6		σ_2		s_6
				So^I	Se^I	So	Se	So^{II}	Se^{II}
	$\sigma_1=s_1+s_3-s_5$	$\delta_1=d_1-d_3-d_5$		$A_1=\frac{So^I+Se^I}{6}$		$A_3=\frac{So+Se}{6}$		$A_5=\frac{So^{II}+Se^{II}}{6}$	
	$\sigma_2=s_2-s_6$	$\delta=d_0-d_4$		$A_{11}=\frac{So^I-Se^I}{6}$		$A_9=\frac{So-Se}{6}$		$A_7=\frac{So^{II}-Se^{II}}{6}$	

	Cosine terms					
	1st and 11th		3d and 9th		5th and 7th	
sin 15°		d_5				d_1
" 30°	d_4				d_4	
" 45°		d_3		δ_1		$-d_3$
" 60°	d_2				$-d_2$	
" 75°		d_1				d_5
" 90°	d_0		δ_2		d_0	
	De^I	Do^I			De^{II}	Do^{II}
	$B_1=\frac{De^I-Do^I}{6}$		$B_3=\frac{\delta_2+\delta_1}{6}$		$B_5=\frac{De^{II}+Do^{II}}{6}$	
	$B_{11}=\frac{De^I-Do^I}{6}$		$B_9=\frac{\delta_2-\delta_1}{6}$		$B_7=\frac{De^{II}-Do^{II}}{6}$	

their sum obtaining the quantity S_0''. Similarly, the quantity S_e'' is found as the sum of the products s_2 sin 30°, $-s_4$ sin 60°, and s_6 sin 90°. In the case of the 12-point schedule the coefficients

TABLE 3

Eighteen Point Schedule

Measured ordinates	Sums	Diffs.		Sine terms								
				1st and 17th		3d and 15th		5th and 13th		7th and 11th		9th
y_0		d_0										
y_1 y_{17}	s_1	d_1	sin 10°	s_1				$-s_7$		$-s_5$		
y_2 y_{16}	s_2	d_2	" 20°		s_2				$-s_4$		$-s_8$	
y_3 y_{15}	s_3	d_3	" 30°	s_3		σ_1		s_3		$-s_3$		
y_4 y_{14}	s_4	d_4	" 40°		s_4				s_8		s_2	
y_5 y_{13}	s_5	d_5	" 50°	s_5				s_1		s_7		
y_6 y_{12}	s_6	d_6	" 60°		s_6		σ_2		$-s_6$		s_6	
y_7 y_{11}	s_7	d_7	" 70°	s_7				$-s_5$		s_1		
y_8 y_{10}	s_8	d_8	" 80°		s_8				s_2		$-s_4$	
y_9	s_9		" 90°	s_9		σ_3		s_9		$-s_9$		Σ
				Se^{I}	Se^{I}	Se^{II}	Se^{II}	Se^{III}	Se^{III}	Se^{IV}	Se^{IV}	
$\sigma_1=s_1+s_5-s_7$				$A_1=\frac{So^{I}+Se^{I}}{9}$		$A_3=\frac{So^{II}+Se^{II}}{9}$		$A_5=\frac{So^{III}+Se^{III}}{9}$		$A_7=\frac{Se^{IV}+Se^{IV}}{9}$		$A_9=\frac{\Sigma}{9}$
$\sigma_2=s_2+s_4-s_8$ $\Sigma=\sigma_1-\sigma_3$												
$\sigma_3=s_3-s_9$				$A_{17}=\frac{Se^{I}-Se^{I}}{9}$		$A_{15}=\frac{Se^{II}-Se^{II}}{9}$		$A_{13}=\frac{Se^{III}-Se^{III}}{9}$		$A_{11}=\frac{Se^{IV}-Se^{IV}}{9}$		

		Cosine terms								
		1st and 17th		3d and 15th		5th and 13th		7th and 11th		9th
	sin 10°	d_8				$-d_2$		d_4		
$\delta_0=d_0-d_6$	" 20°		d_7				$-d_5$		d_1	
	" 30°	d_6		δ_2		d_6		d_6		
$\delta_1=d_1-d_5-d_7$	" 40°		d_5				d_1		$-d_7$	
$\delta_2=d_2-d_4-d_8$	" 50°	d_4				d_8		$-d_2$		
	" 60°		d_3		δ_1		$-d_3$		$-d_3$	
$\Delta=\delta_0-\delta_2$	" 70°	d_2				$-d_4$		$-d_8$		
	" 80°		d_1				d_7		d_5	
	" 90°	d_0		δ_0		d_0		d_0		Δ
		De^{I}	De^{I}	De^{II}	De^{II}	De^{III}	De^{III}	De^{IV}	De^{IV}	
		$B_1=\frac{De^{I}+De^{I}}{9}$		$B_3=\frac{De^{II}+De^{II}}{9}$		$B_5=\frac{Do^{III}+De^{III}}{9}$		$B_7=\frac{De^{IV}+De^{IV}}{9}$		$B_9=\frac{\Delta}{9}$
		$B_{17}=\frac{De^{I}-De^{I}}{9}$		$B_{15}=\frac{De^{II}-De^{II}}{9}$		$B_{13}=\frac{Do^{III}-De^{III}}{9}$		$B_{11}=\frac{De^{IV}-De^{IV}}{9}$		

A_3, A_9, B_3, and B_9 involve several of the differences d_m and the sums s_m in each of the products. Thus, in the case of the 12-point schedule, the quantity $\sigma_1 = s_1 + s_3 - s_5$ has to be multiplied by sin 45° as also the quantity $\delta_1 = d_1 - d_3 - d_5$. These schedules will be further explained and illustrated by numerical examples below.

To aid in making the numerical calculations, there have been tabulated (Appendix A) the products of all the sines which enter into these schedules by all the whole numbers up to 100. These products are carried out to three decimal places. Interpolation is accomplished by means of the same table by simply shifting the decimal point. Thus, any product of an ordinate of four figures may be found by entering the table twice and making a simple addition. For example, the product of the ordinate 74.39 by sin 70° is found by entering column 7 of the table with argument 74 and 39. The numbers found are 69.538 and 36.648. The required product is therefore 69.538 + .366 = 69.904. Those products which involve sin 30° and sin 90° will of course be obtained without the aid of the table.

In work of this kind some check on the accuracy of the numerical work is almost indispensable. Fortunately, such a check may be made without any considerable amount of labor. The equations below give sufficient relations between the coefficients and the measured ordinates to establish the correctness of the values of the coefficients derived by calculations.

2. CHECKS ON THE ACCURACY OF THE CALCULATIONS

Check on the 6-point Analysis

$$
\begin{aligned}
y_0 &= (B_1 + B_5) + B_3 \\
y_3 &= (A_1 + A_5) - A_3 \\
s_2 &= 2(A_1 - A_5) \sin 60^\circ \\
d_1 &= 2(B_1 - B_5) \sin 60^\circ
\end{aligned}
\qquad (10)
$$

Check on the 12-point Analysis

$$
\begin{aligned}
y_0 &= (B_1 + B_{11}) + (B_3 + B_9) + (B_5 + B_7) \\
y_6 &= (A_1 - A_{11}) - (A_3 - A_9) + (A_5 - A_7) \\
s_3 &= 2 \sin 45^\circ . [(B_1 - B_{11}) - (B_3 - B_9) - (B_5 - B_7)] \\
d_3 &= 2 \sin 45^\circ . [(A_1 + A_{11}) + (A_3 + A_9) - (A_5 + A_7)] \\
d_2 &= 2 \sin 60^\circ . [(B_1 + B_{11}) - (B_5 + B_7)] \\
s_4 &= 2 \sin 60^\circ . [(A_1 - A_{11}) - (A_5 - A_7)]
\end{aligned}
\qquad (11)
$$

Of the equations (11) the first gives a check on the sums of the complementary B coefficients, while the second gives an indication of the accuracy of the differences of the complementary A coefficients. If the third and fourth of the equations are also satisfied the check is complete, since when the sums and differences of the complementary coefficients have been shown to be correct the individual coefficients must necessarily be correct. In case of the failure of the calculated values to satisfy any one of the equations, it is difficult to determine from the equations wherein the trouble lies. Herein the check for the 12-point analysis is not so convenient as that for the 6-point analysis. The last two equations in (11) have accordingly been appended to aid in such a case, since they do not contain the coefficients A_3, A_9, B_3, or B_9.

Check on the 18-point Analysis

$$\left.\begin{aligned}
y_0 &= (B_1+B_{17})+(B_3+B_{15})+(B_5+B_{13})+(B_7+B_{11})+B_9\\
y_9 &= (A_1+A_{17})+(A_5+A_{13})+A_9-(A_3+A_{15})-(A_7+A_{11})\\
d_3 &= 2\sin 60^\circ.[(B_1-B_{17})-(B_5-B_{13})-(B_7-B_{11})]\\
s_6 &= 2\sin 60^\circ.[(A_1-A_{17})-(A_5-A_{13})+(A_7-A_{11})]
\end{aligned}\right\}\quad(12)$$

The first two of the equations (12) should first be applied. If these are satisfied, the sums of all the complementary coefficients are correct, which shows that the quantities S_0 and D_0 have been correctly computed. Similarly, the third equation is a check on the accuracy of the calculation of the quantities D_6 upon which the differences of the complementary B coefficients depend, while the fourth equation gives the corresponding check on the quantities S_6. The system of control shown in equations (10), (11), and (12) gives not only a complete check on the calculation of the coefficients, but in case of error serves to indicate within comparatively narrow limits what part of the work needs to be examined for error. The only combinations of coefficients which do not enter into the check equations (12) are the differences of the third and fifteenth harmonics, and the calculation of these is so simple that it is best to take the few moments necessary to repeat the calculation of these quantities. Since the products involved in $A_3-A_{15}=S_6''$ and $B_3-B_{15}=D_6''$ contain sin 30° and sin 90° only, the chances of error in taking the products is no greater than that in applying any of the equations (12).

It is recommended that every analysis be checked. In spite of the fact that simple arithmetical operations only enter into the analysis, errors very easily slip in, which are readily detected on carrying through the check, and in any case the small amount of time necessary to apply the check is amply repaid by the added confidence thus lent to the results of the analysis.

3. CALCULATION OF THE AMPLITUDE AND PHASE OF THE HARMONICS

Having obtained and checked the values of the coefficients A_k and B_k in the Fourier equation (2), it still remains to calculate from these coefficients the amplitudes and phase relations of the different harmonics. For this purpose, we designate by C_k the amplitude of the kth harmonic and by θ_k the difference of phase between this harmonic and the arbitrary phase of reference, which is that of the ordinate chosen as y_0. Putting $A_k = C_k \cos \theta_k$ and $B_k = C_k \sin \theta_k$ we have in general

$$\begin{aligned} A_k \sin kpt + B_k \cos kpt &= C_k \sin (kpt - \theta_k) \\ &= C_k \sin k(pt - \psi_k) \end{aligned} \tag{13}$$

where

$$C_k = \sqrt{A_k^2 + B_k^2}$$

$$\tan \theta_k = \frac{-B_k}{A_k} \qquad \psi_k = \frac{\theta_k}{k}$$

The quadrant of θ_k is uniquely determined from the consideration that the algebraic signs of the numerator and denominator in the equation for tan θ_k are respectively those of sin θ_k and cos θ_k. The phase of any harmonic C_k with respect to the fundamental, expressed in terms of the period of the latter, is given by $(\theta_1 - \psi_k)$, or we may displace the origin so as to refer the whole curve to the zero point of the fundamental by making $\theta_1 = 0$, and subtracting θ_1 from the value of ψ_k for each harmonic. The angle θ_k expresses the difference in phase between the harmonic and the point of reference, but in terms of the period of the harmonic itself. It is convenient to use θ_k or ψ_k according to circumstances.

4. CHOICE OF THE SCHEDULE TO BE USED

Using the schedules detailed above, the analysis of a curve may be easily and expeditiously carried out. As an indication of the amount of labor required, the number of entries which must be made in the multiplication table is as follows: 6-point, 2; 12-point, 14; and for the 18-point schedule, 40. The additions and subtractions require, in any given case, about half as much time as the multiplications. The total length of time necessary for calculating the coefficients may be estimated as less than 10 minutes for a 6-point analysis, and about three-quarters of an hour for an 18-point analysis.

The question naturally arises as to the choice of schedule in any given case. This depends, of course, both on the nature of the curve and on the precision desired. For example, if the curve be free from ripples of short period, and closely approximates in appearance to a sine wave, it will be sufficient to take into account nothing higher than the fifth harmonic, and the 6-point schedule will be chosen. On the contrary, if the curve be more or less irregular, and especially if the sinuosities are of short period compared with the fundamental, it will be necessary to carry out the analysis to include higher harmonics. However, it is not always easy to judge what higher-order terms should be looked for. It very often occurs that several harmonics may be present to nearly an equal degree, in which case the curve will show a peak wherever the maxima of these harmonics come nearly together, and a trough in those regions where they reach their negative maxima simultaneously. In such cases only a very imperfect idea can be gained, by mere inspection, of the number and nature of the harmonics present. In the case of slotted armatures one can predict with a good deal of certainty that certain harmonics should be present in the emf. wave. For example, if an armature have 13 slots per pair of poles in the field, it is probable that the thirteenth harmonic will be present to a notable extent in the emf. wave; if there be 12 slots per pair of poles, then the eleventh and thirteenth harmonics are to be expected.

To be absolutely certain, in a given case, that no harmonic of higher order than those included in the analysis is present to an appreciable extent, it is necessary to compute from the calculated coefficients the values of the ordinates of the curve for points other than those used in the analysis, and to compare the values thus obtained with the actual measured values at these points. For this test enough points should be included to avoid the possibility of considering only those places where the harmonics to be detected nearly annul each other, or are near their minimum values. The matter is somewhat complicated by the fact that with harmonics present of higher order than those included in the analysis, the value of the highest harmonic actually calculated comes out, not with its true value, but of such a magnitude as to correct for the effects of yet higher harmonics at the phases of the fundamental ordinates.

The calculation of the ordinates of points intermediate to those included in the analysis, using the values of the harmonics derived by an analysis, may be simplified by properly choosing the ordinates for which the calculation is to be made. The derivation of the schemes of calculation given in the following table is a simple matter; the nomenclature is the same as in the preceding pages.

The phases of the ordinates which may be calculated by Table 4 are indicated by subscripts. For example, the ordinate y_{50}, in the middle section of the table lies 50° away from the fundamental ordinate y_0 used in the analysis. The table indicates that the value of y_{50} which is consistent with the results of the analysis is to be found by performing certain operations on the coefficients which have been found by the analysis. Thus, A_3 is to be multiplied by sin 30°, $-A_5$ by sin 70°, etc. These products are arranged in two groups whose sums M_s and N_s are then to be found. The sum (M_s+N_s) gives the required value of y_{50}, and the difference (M_s-N_s), the value of its complementary ordinate y_{130}. On comparing these calculated values with the actual ordinates of the curve, an idea of the adequacy of the analysis is obtained.

It will sometimes occur that more or less complete resonance of a harmonic of high frequency will exist, and will give the wave a rippled appearance such as to allow the order of the resonant harmonic to be established with certainty. For example, if it is practically certain from the frequency of the ripples that a component emf. of a frequency 21 times that of the fundamental is present, the magnitude and phase of this harmonic may be obtained by measuring 22 equidistant points per half wave, and

TABLE 4

For the Calculation of the Ordinates of Points Intermediate to Those Used in the Analysis

SIX-POINT SCHEDULE

sin 15°	A_1	B_5			A_5	B_1
" 45°	A_3	B_3	$(A_1+A_3-A_5)$	$(B_1-B_3-B_5)$	$-A_3$	$-B_3$
" 75°	A_5	B_1			A_1	B_5
Sums	M_1	N_1	M_2	N_2	M_3	N_3
	$y_{15}=M_1+N_1$		$y_{45}=M_2+N_2$		$y_{75}=M_3+N_3$	
	$y_{165}=M_1-N_1$		$y_{135}=M_2-N_2$		$y_{105}=M_3-N_3$	

TWELVE-POINT SCHEDULE

sin 10°	A_1			$-B_5$		(B_7+B_{11})	$-(A_7+A_{11})$		$-A_5$			B_1
" 20°		(B_7-B_{11})	A_1		$-A_5$			$-B_5$		B_1	$-(A_7+A_{11})$	
" 30°	A_3			B_3		$-B_3$	A_3		$-A_3$			$-B_3$
" 40°		B_5	(A_7-A_{11})		A_1			B_1		$-(B_7-B_{11})$	A_5	
" 50°	A_5			$-(B_7+B_{11})$		B_1	A_1		(A_7+A_{11})			B_5
" 60°		B_3	A_3		A_3			$-B_3$		$-B_3$	$-A_3$	
" 70°	(A_7+A_{11})			B_1		$-B_5$	$-A_5$		A_1			$-(B_7+B_{11})$
" 80°		B_1	A_5		$-(A_7-A_{11})$			(B_7-B_{11})		B_5	A_1	
" 90°	A_9			$-B_9$		B_9	A_9		$-A_9$			B_9
Sums	M_1	N_1	M_2	N_2	M_4	N_4	M_5	N_5	M_7	N_7	M_8	N_8
M+N	y_{10}		y_{20}		y_{40}		y_{50}		y_{70}		y_{80}	
M−N	y_{170}		y_{160}		y_{140}		y_{130}		y_{110}		y_{100}	

EIGHTEEN-POINT SCHEDULE

sin 15°	a_1	b_5			a_5	b_1
" 45°	a_3	b_3	α	β	$-a_3$	$-b_3$
" 75°	a_5	b_1			a_1	b_5
Sums	M_1	N_1	α	β	M_3	N_3
	$y_{15}=M_1+N_1$		$y_{45}=\alpha+\beta$		$y_{75}=M_3+N_3$	
	$y_{165}=M_1-N_1$		$y_{135}=\alpha-\beta$		$y_{105}=M_3-N_3$	

where

$a_1=A_1+A_{11}-A_{13}$ $\quad b_1=B_1-B_{11}-B_{13}$ $\quad \alpha=a_1+a_3-a_5$

$a_3=A_3+A_9-A_{15}$ $\quad b_3=B_3-B_9-B_{15}$ $\quad \beta=b_1-b_3-b_5$

$a_5=A_5+A_7-A_{17}$ $\quad b_5=B_5-B_7-B_{17}$

calculating the values of A_{21} and B_{21} directly by means of equation (7). It is well in such a case to recalculate the harmonic from other sets of 22 ordinates, since it is hard to be sure that other harmonics of nearly the same frequency are not also present. See example 3.

Evidently, in case of doubt, such tests require about as much time as the analysis itself, so that it will generally be well to err on the safe side, and select that schedule of analysis, which will certainly include all those harmonics which are reasonably to be expected. A second analysis using the same schedule, but with a different set of ordinates will if in good agreement prove that the neglected harmonics are negligible. Fortunately, in the great majority of cases, harmonics of order higher than the fifteenth are of rare occurrence, and only in the case of resonance will the value of these upper harmonics be appreciable.

IV. EXAMPLES OF THE USE OF THE ANALYSIS SCHEDULES

EXAMPLE 1. ANALYSIS OF A CURVE BY THE SIX-POINT SCHEDULE

As an example of the application of the 6-point schedule we may take the curve A, Fig. 1, which shows the current wave in a highly inductive circuit. This curve approximates very closely a simple sine wave in its appearance, and no appreciable harmonics of high order are to be expected.

The fundamental ordinates used, which are the means of those of two consecutive half waves are as follows:

$y_0 = -1.3$ $\qquad d_0 = -1.3$
$y_1 = 15.1 \qquad y_5 = 17.3 \qquad s_1 = 32.4 \qquad d_1 = -2.2$
$y_2 = 28.0 \qquad y_4 = 28.85 \qquad s_2 = 56.85 \qquad d_2 = -0.85$
$y_3 = 32.35 \qquad s_3 = 32.35$

The average deviations of the pairs of measured ordinates from their means was about 0.4 of a unit on the same scale, which difference is mainly due to the fact that the zero line of the paper was slightly displaced from the actual line of zero electromotive force.

The analysis is given in full in Table 5, together with the check given in equations (10). Italic type indicates that part of the work which could be saved by the use of a printed form. In the column at the extreme left are given the numbers of the rows.

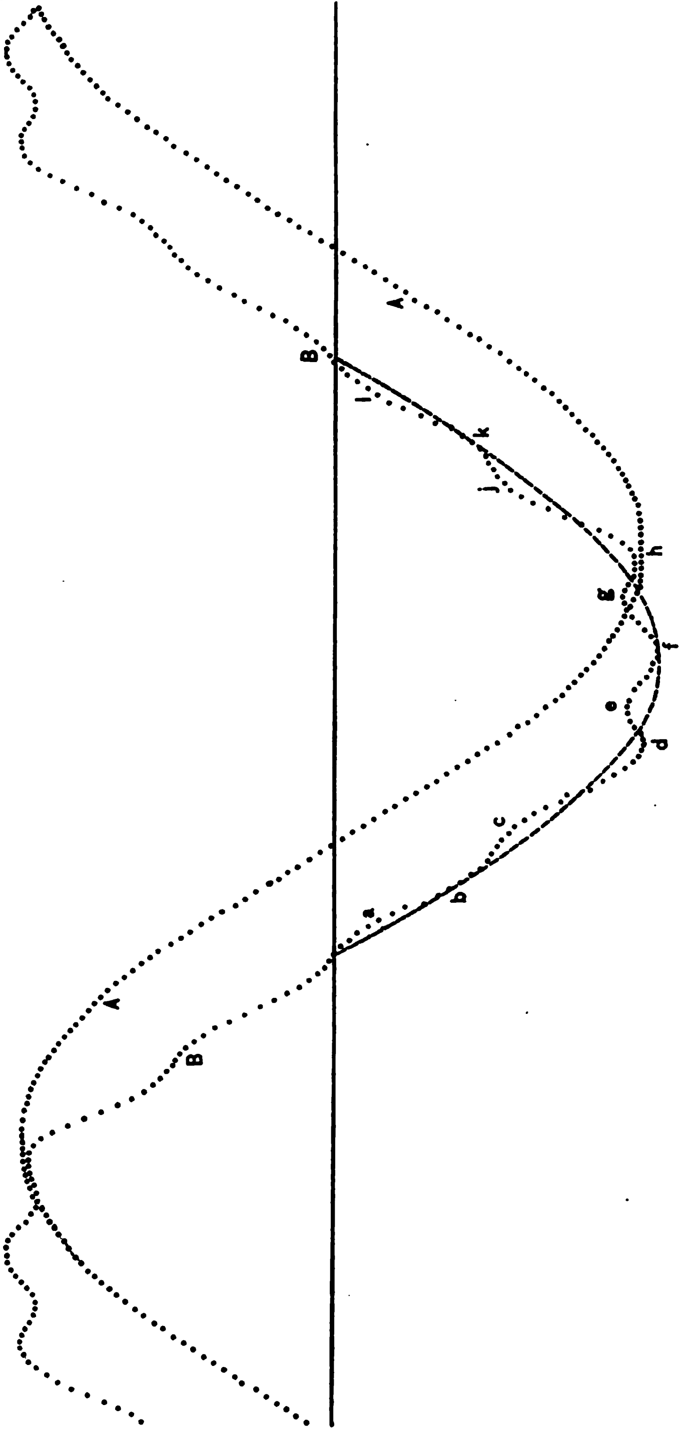

Fig. 1.—*Curve A, current in a highly inductive circuit. Curve B, electromotive force, curve producing the current, curve A*

In the second part of the table is shown the calculation of the check ordinates. The greatest deviation between any fundamental ordinate, and its value calculated from the coefficients A_m and B_m is .002, a concordance which may be regarded as satisfactory. The entire work has been carried out to a greater number

TABLE 5

Analysis of a Curve from Six Ordinates

	Measured ordinates	*s.*	*d.*	*Sine terms*			*Cosine terms*		
				1st and 5th		*3d*	*1st and 5th*		*3d*
				+ −	+ −		+ −	+ −	
0	−1.3		−1.3						
1	15.1 17.3	32.4	−2.2	16.200			0.425		
2	28.0 28.85	56.85	−0.85		49.233	32.400		1.905	−1.300
3	32.85	32.85		32.350		32.350	1.300		0.850
			Sums	49.550	49.233	0.050	1.725	1.905	−0.450
			S_e	49.233			1.905		
				97.783	−0.683		−3.630	0.180	
			$A_1=$	32.594	$A_5=-0.228$	$A_3=0.017$	$B_1=-1.210$	$B_5=0.060$	$B_3=-0.150$

CHECK

B_1+B_5	−1.150	A_1+A_5	32.366	(A_1-A_5)	32.822	(B_1-B_5)	−1.270
B_0	−0.150	$-A_3$	−0.017	$\times 2$	65.644	$\times 2$	−2.540
Sum	−1.300	*Sum*	32.349		56.291		−2.165
y_0	−1.3	y_3	32.85		.554		.035
					.008		
$A_1+A_5=32.366$				$2(A_1-A_5)$	56.848	$2(B_1-B_5)$	−2.200
$A_1-A_5=32.822$				× sin 60°		× sin 60°	
$B_1+B_5=-1.150$				s_2	56.85	d_1	−2.2
$B_1-B_5=-1.270$							

CALCULATION OF THE AMPLITUDES AND PHASES

$C_1=\sqrt{\overline{32.594}^2+\overline{1.210}^2}$	$C_5=\sqrt{\overline{0.017}^2+\overline{0.150}^2}$	$C_3=\sqrt{\overline{0.228}^2+\overline{0.060}^2}$
$=32.616$	$=0.151$	$=0.236$
$\tan\theta_1=\frac{1.210}{32.594}$	$\tan\theta_5=\frac{0.150}{0.017}$	$\tan\theta_3=\frac{-0.060}{-0.228}$
$=0.0371$	$=8.8$	$=0.263$
$\theta_1=2°\ 8'$	$\theta_5=83°.5$	$\theta_3=194°.7$
	$\phi_5=27°.8$	$\phi_3=38°.9$

Example of Anal

	Measured ordinates		s	d	
0	0.3			0.3	+
1	8.5	8.7	17.2	−0.2	4.452
2	14.3	18.4	32.7	−4.1	
3	20.6	26.0	46.6	−5.4	32.951
4	26.15	30.7	56.85	−4.55	
5	29.8	32.9	62.7	−3.1	60.564
6	32.25		32.25		
				Sums	97.967
				S_o	97.967
				S_e	97.833
				Amplitudes	A_1

σ_1	σ_2	0	+
17.2	32.7	1	
46.6	32.25	2	
63.8	0.45	3	
62.7		4	
1.1		5	
		6	0.300
δ_1	δ_2	Sums	0.300
		D_o	−5.526
−0.2	0.3	D_e	−4.813
5.4	4.55		−10.339
3.1			
8.3	4.85	Amplitudes	B_1

	+	−	
B_1+B_{11}		1.842	A_1-A_{11}
B_3+B_9	1.616		$-(A_3-A_9)$
B_5+B_7	0.525		A_5-A_7.
	2.141	1.842	
	1.842		
y_0	0.299		y_6
Actual value	0.3		Actual value

CALCU

$C_1 = \sqrt{32.633^2 +}$

$C_3 = \sqrt{0.205^2 +}$

$C_5 = \sqrt{0.124^2 +}$

$C_7 = \sqrt{0.087^2 +}$

$C_9 = \sqrt{0.055^2 +}$

$C_{11} = \sqrt{0.119^2 +}$

of significant figures than the accuracy of the curve and the errors of reading the ordinates warrant, since it was desired to illustrate the work using the full number of places given in the multiplication table. If a smaller number of significant figures be retained, the labor is correspondingly reduced.

In the last part of the table are given the values of the amplitudes and phase differences calculated from equations (13). For the calculation of the amplitudes a table of squares and square roots will be found a material aid; the calculation of the phase differences is simplified by the use of a slide rule and a table of natural tangents.

The given curve is represented by the equation

$$I = 32.616 \sin (pt - 2^\circ\ 8') + 0.151 \sin 3(pt - 27^\circ.8) + 0.236 \sin 5(pt - 38^\circ.9) \text{ division}$$

in terms of the arbitrary scale used, or since 20 divisions = 0.5 amperes.

$$I = 0.8154 \sin (pt - 2^\circ\ 8') + 0.00378 \sin 3(pt - 27^\circ.8) + 0.00590 \sin 5(pt - 38^\circ.9) \text{ amperes.}$$

With the origin chosen, the phase of the ordinate y_0 lies 2° 8′ to the left of the zero point of the fundamental. The equation referred to the latter is accordingly

$$I = 0.8154 \sin pt + 0.00378 \sin 3(pt - 25^\circ.7) + 0.00590 \sin 5(pt - 36^\circ.8) \text{ amperes.}$$

EXAMPLE 2. ANALYSIS OF A CURVE BY THE TWELVE-POINT SCHEDULE

In Table 6 is given the complete analysis of one of the emf waves of a small two-phase generator, curve B, Fig. 2. Although the curve is noticeably different from a pure sine wave, no irregularities of very high period are apparent, and the 12-point schedule was used.

The equation of the curve found is

$$E = 32.678 \sin (pt - 3^\circ 2') + 1.798 \sin 3(pt - 92^\circ.2) + 0.410 \sin 5(pt - 50^\circ.5) + 0.160 \sin 7(pt - 43^\circ.3) + 0.179 \sin 9(pt - 8^\circ.0) + 0.121 \sin 11(pt - 7^\circ.2) \text{ divisions.}$$

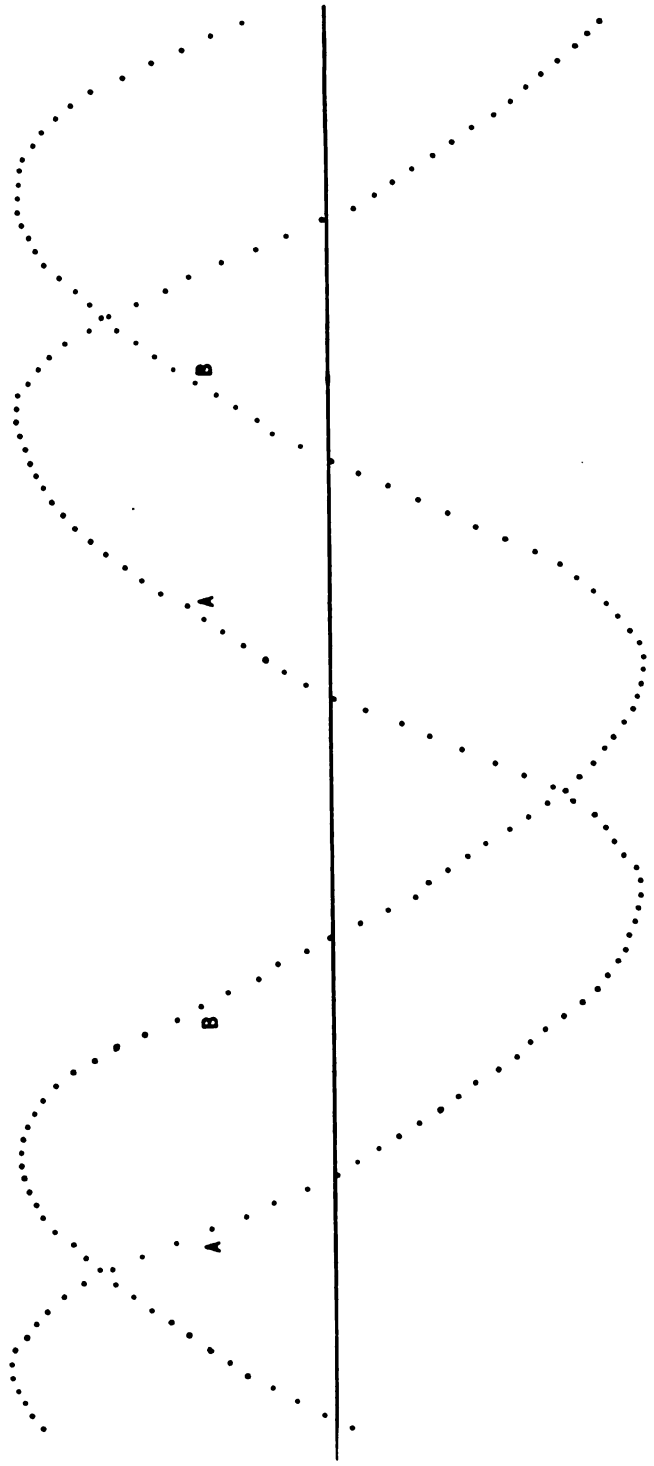

Fig. 2.—*Curves of electromotive force of small two-phase machine*

EXAMPLE 3. ANALYSIS OF A CURVE BY THE EIGHTEEN-POINT SCHEDULE

The curve A, Fig. 3, is that of the emf. wave of a small generator having 14 slots per pair of poles. This would lead one to expect appreciable harmonics of the thirteenth and fifteenth orders. That this was actually the case is evidenced by the ripples of high frequency on the side of the curve. The curve was, accordingly, analyzed using the 18-point schedule. The complete calculation is shown in Table 7. Although the amount of work is greater than in the two preceding examples, nothing new presents itself.

The results of the analysis show that the amplitudes of the thirteenth and fifteenth harmonics have values as great as several per cent of the fundamental, and are exceeded by the amplitudes of no other harmonics with the exception of the fifth.

The complete equation found is

$$
\begin{gathered}
E = 33.217 \sin (pt - 1^\circ\ 36') + 0.970 \sin 3(pt - 2^\circ.1) \\
+ 1.702 \sin 5(pt - 41^\circ 8) \\
+ 0.218 \sin 7(pt - 38^\circ 3) + 0.355 \sin 9(pt - 2^\circ 3) \\
+ 0.205 \sin 11(pt - 19^\circ 3) \\
+ 1.251 \sin 13(pt - 3^\circ 8) + 1.528 \sin 15(pt - 15^\circ 7) \\
+ 0.159 \sin 17(pt - 3^\circ 0)
\end{gathered}
$$

which shows that, for this curve, an analysis using only 6 points or 12 points would be insufficient.

EXAMPLE 4. CHOICE OF SCHEDULE

In order to illustrate what has been said with respect to the choice of schedule to be used in any given instance, the analysis of each of the three curves in the preceding examples has been carried through with each of the three schedules given here, the results of these analyses being set forth in Table 8.

From this table we see that, for the curve in Example 1, the analysis from 6 points is sufficient for all purposes, the amplitudes of the higher harmonics, found by carrying out the analysis to include more points, are of the order of magnitude of the errors in reading the ordinates, and are not to be regarded as of practical significance. Errors in the curve, due to slight progressive variations in the voltage generated by the machine, where not averaged

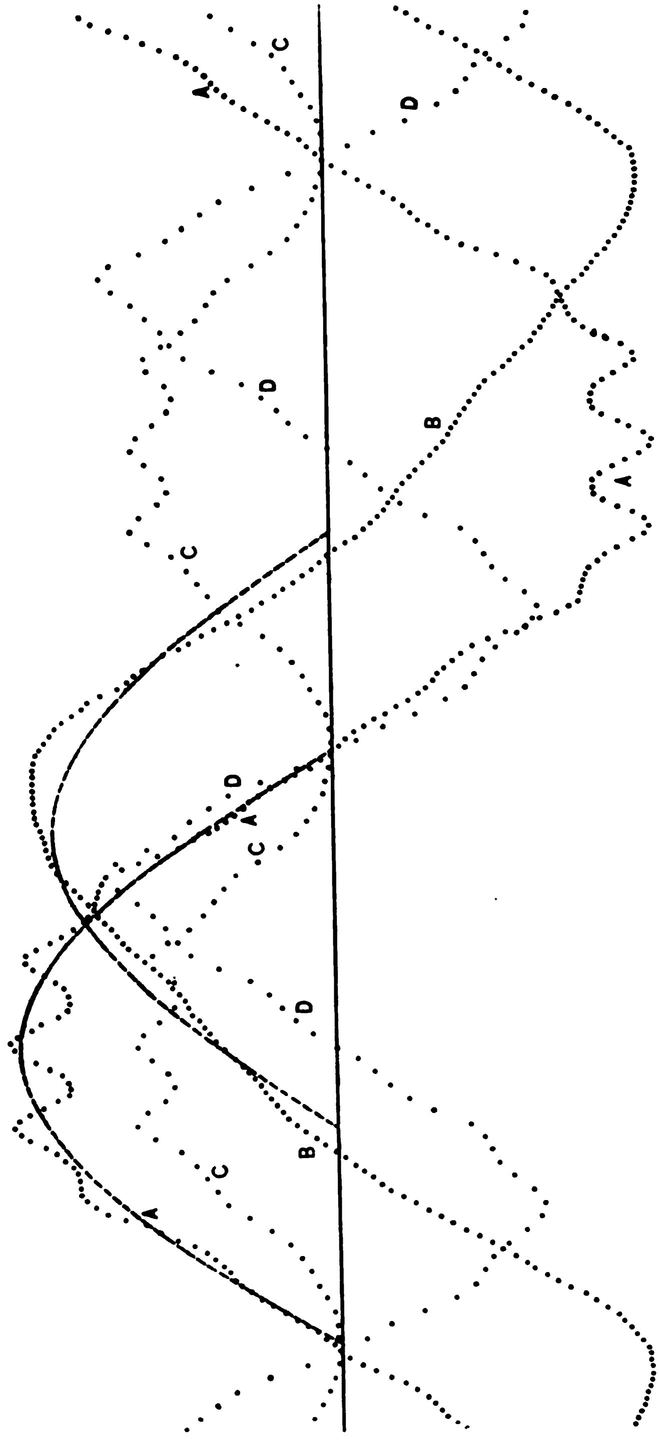

FIG. 3.—*Curve A, curve of electromotive force impressed on primary of transformer. Curve B, magnetising current. Curve C, power used in hysteresis and eddy currents. Curve D, wattless component of the power*

D_0	-4.724	
D_e	-3.604	
	-8.328	-1.120
Amplitudes	$B_1=-0.925$	$B_{17}=-0.124$

	+	−	
B_1+B_{17}		1.049	A_1+A_{17}
B_3+B_{15}	1.156		$-(A_3+A_{15}$
B_5+B_{13}		0.210	A_5+A_{13}
B_7+B_{11}	0.326		$-(A_7+A_{11}$
B_9		0.122	A
Sums	1.482	1.381	*Sum*
$y_0=$	0.101		1
Actual value	0.1		*Actual valu*

CALC

$C_1=\sqrt{33.20}$

$C_3=\sqrt{0.96}$

$C_5=\sqrt{1.53}$

$C_7=\sqrt{0.0}$

$C_9=\sqrt{0.3}$

$C_{11}=\sqrt{0.1}$

$C_{13}=\sqrt{0.8}$

$C_{15}=\sqrt{0.8}$

$C_{17}=\sqrt{0.}$

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TABLE 8

Comparison of the Results of Analyses of the Same Curves Using Different Numbers of Ordinates

Curve of Example 1

	6 points	12 points	18 points		6 points	12 points	18 points
C_1	32.616	32.641	32.648	ϕ_1	2°8′	1°55′	1°32′
C_3	0.151	0.103	0.096	ϕ_3	27°.8	26°.5	35°.5
C_5	0.236	0.291	0.288	ϕ_5	38°.9	36°.2	37°.0
C_7		0.085	0.082	ϕ_7		30°.8	29°.0
C_9		0.073	0.075	ϕ_9		12°.8	15°.4
C_{11}		0.108	0.124	ϕ_{11}		61°.8	5°.5
C_{13}			0.019	ϕ_{13}			6°.5
C_{15}			0.032	ϕ_{15}			3°.3
C_{17}			0.011	ϕ_{17}			11°.2

Curve of Example 2

	6 points	12 points	18 points		6 points	12 points	18 points
C_1	32.663	32.678	32.773	ϕ_1	3°14′	3°2′	3°22′
C_3	1.623	1.798	1.775	ϕ_3	91°.8	92°.2	93°.1
C_5	0.566	0.410	0.507	ϕ_5	49°.6	50°.5	51°.8
C_7		0.160	0.183	ϕ_7		43°.3	44°.3
C_9		0.179	0.221	ϕ_9		8°.0	6°.8
C_{11}		0.121	0.180	ϕ_{11}		7°.2	0°.8
C_{13}			0.145	ϕ_{13}			24°.4
C_{15}			0.064	ϕ_{15}			16°.4
C_{17}			0.113	ϕ_{17}			5°.0

Curve of Example 3

	6 points	12 points	18 points		6 points	12 points	18 points
C_1	34.240	33.194	33.217	ϕ_1	2°50′	1°42′	1°36′
C_3	1.059	1.051	0.970	ϕ_3	85°.8	−0°.8	2°.1
C_5	1.653	1.680	1.702	ϕ_5	42°.3	40°.2	41°.7
C_7		0.268	0.218	ϕ_7		34°.1	38°.3
C_9		1.619	0.355	ϕ_9		−4°.2	2°.2
C_{11}		1.279	0.205	ϕ_{11}		13°.0	19°.3
C_{13}			1.251	ϕ_{13}			3°.8
C_{15}			1.528	ϕ_{15}			15°.7
C_{17}			0.159	ϕ_{17}			9°.0

out by taking two half waves, affect all the analyses in nearly the same way, especially since the fundamental ordinates used are in part common to all three analyses. Sudden fluctuations of short duration tend to give spurious values for the higher harmonics. Such can, however, be detected by repeating the analyses using other sets of ordinates, as shown in example 5 below.

In the case of the curve of Example 2, the analysis from six points gives a very satisfactory degree of accuracy for the third and fifth harmonics, but the amplitudes of the seventh, ninth and eleventh harmonics, found by using more points, are greater than in some cases could be neglected.

In the case of the curve in Example 3, neither the 6-point nor the 12-point analysis is sufficient. In the former the amplitude of the fundamental and the phase of the third harmonic are considerably in error; in the latter, neglecting the thirteenth and fifteenth harmonics, gives erroneous values for the ninth and eleventh harmonics.

The inadequacy of the 6-point and 12-point analyses, in Example 3, may be further shown by calculating the values of the ordinates of points not used in the analyses for comparison with the actual values taken from the curve. Thus, from the schedules of Table 4, the values given in the following table were calculated. The

TABLE 9

Calculated Values of Ordinates of Curve in Example 3 for Points not Used in the Analyses

18 points				6 points				12 points			
Phase	Ordinates		Differences	Phase	Ordinates		Differences	Phase	Ordinates		Differences
	Observed	Calculated			Observed	Calculated			Observed	Calculated	
15°	7.55	7.49	+0.06	15°	7.55	7.02	+0.53	10°	4.6	4.75	−0.15
45°	25.85	25.83	+0.02	45°	25.85	23.99	+1.86	20°	10.2	9.61	+0.59
75°	29.95	30.64	−0.69	75°	29.95	31.54	−1.59	40°	22.25	22.43	−0.18
105°	28.0	27.68	+0.32	105°	28.0	30.45	−2.45	50°	26.8	27.08	−0.28
135°	25.35	25.10	+0.25	135°	25.35	26.50	−1.15	70°	33.4	30.91	+2.49
165°	9.1	9.08	+0.02	165°	9.1	8.57	+0.53	80°	28.1	30.86	−2.76
								100°	30.8	30.80	0
								110°	28.4	30.12	−1.72
								130°	26.4	28.37	−1.97
								140°	24.75	22.63	+2.12
								160°	11.2	11.97	−0.77
								170°	6.3	5.73	+0.57

phases of the various points refer to the same origin as was used in the analyses.

With the exception of one point, the calculated and actual values of these ordinates, using the 18-point analysis, are in satisfactory agreement; the deviations in the case of the 6-point and 12-point analysis are, however, very appreciable, and the 12-point analysis has very little advantage in this respect over the 6-point.

The deviations were also calculated for the curve in Example 2, but were not greater than about 0.5 division in the case of all three analyses, the agreement being no better when 18 points were used than with only 6. This procedure does not, therefore, give much information, except when the neglected harmonics are of relatively large importance. It will generally be found that a decision regarding the sufficiency of any given analysis will be more rapidly and certainly reached by carrying through another analysis, using the same schedule, but with an independent set of ordinates.

EXAMPLE 5. ACCURACY OF RESULTS

To throw light on the question as to what precision has been reached in the preceding examples, analyses were made using other sets of ordinates than those on which these examples were based. The results are given in Table 10. The different sets of ordinates are distinguished by reference to the relative phases of y_0 referred to the zero points of the preceding analyses.

TABLE 10

Comparison of Results of Analyses of Same Curves Using Different Sets of Ordinates

CURVE OF EXAMPLE 1

6-point analyses											
	0°	2°	4°	6°	8°		0°	2°	4°	6°	8°
C_1	32.616	32.623	32.607	32.653	32.622	ϕ_1	2°8′	2°4′	2°3′	1°52′	1°52′
C_3	0.151	0.118	0.186	0.061	0.151	ϕ_3	27°.8	29°.2	30°.6	19°.6	40°.2
C_5	0.236	0.260	0.218	0.209	0.270	ϕ_5	38.9	36.1	36°.0	34.7	30°.3

TABLE 10—Continued

12-point analyses

	0°	2°	4°	6°	8°		0°	2°	4°	6°	8°
C_1	32.641	....	....	32.605	....	ϕ_1	1°55′	....	....	1°46′	....
C_3	0.108	....	....	0.028	....	ϕ_3	26°.5	....	....	33.3	....
C_5	0.291	....	....	0.317	....	ϕ_5	30°.2	....	....	36.1	....
C_7	0.085	....	....	0.122	....	ϕ_7	30.8	....	....	27.9	....
C_9	0.073	....	....	0.074	....	ϕ_9	12.8	....	....	22.5	....
C_{11}	0.108	....	....	0.088	....	ϕ_{11}	5.6	....	....	12.7	....

CURVE OF EXAMPLE 2

12-point analyses						16-point analyses					
	0°	4°		0°	4°		0°	4°		0°	4°
C_1	32.678	32.658	ϕ_1	3°2′	2°59′	C_1	32.733	32.690	ϕ_1	3°22′	2°51′
C_3	1.798	1.839	ϕ_3	92°.2	92°.4	C_3	1.775	1.814	ϕ_3	93°.1	91°.6
C_5	0.410	0.346	ϕ_5	50.5	48.5	C_5	0.507	0.401	ϕ_5	51°.8	51.6
C_7	0.160	0.053	ϕ_7	43.3	39.9	C_7	0.183	0.061	ϕ_7	44.3	44.6
C_9	0.179	0.137	ϕ_9	8.0	1.2	C_9	0.221	0.077	ϕ_9	6.8	2.1
C_{11}	0.121	0.179	ϕ_{11}	7.2	2.3	C_{11}	0.180	0.104	ϕ_{11}	0.8	2.6
						C_{13}	0.145	0.006	ϕ_{13}	24.4	28.2
						C_{15}	0.064	0.020	ϕ_{15}	16.4	20.3
						C_{17}	0.113	0.047	ϕ_{17}	5.0	8.0

CURVE OF EXAMPLE 3

12-point analyses						18-point analyses					
	0°	6°		0°	6°		0°	6°		0°	6°
C_1	33.194	33.187	ϕ_1	1°42′	1°28′	C_1	33.217	33.202	ϕ_1	1°36′	1°36′
C_3	1.051	0.972	ϕ_3	−0°.8	5°.9	C_3	0.970	1.025	ϕ_3	2°.1	3°.6
C_5	1.680	1.765	ϕ_5	40.2	40.8	C_5	1.702	1.692	ϕ_5	41.7	40.4
C_7	0.268	0.339	ϕ_7	34.1	36.8	C_7	0.218	0.346	ϕ_7	38.3	37.3
C_9	1.619	1.728	ϕ_9	35.8	9.0	C_9	0.355	0.450	ϕ_9	2.2	5.0
C_{11}	1.279	1.801	ϕ_{11}	13.0	24.6	C_{11}	0.205	0.126	ϕ_{11}	19.3	20.5
						C_{13}	1.251	1.275	ϕ_{13}	3.8	3.5
						C_{15}	1.528	1.507	ϕ_{15}	15.7	15.3
						C_{17}	0.159	0.064	ϕ_{17}	3.0	17.8

An examination of the table shows that analyses depending on different sets of ordinates give the amplitudes of harmonics, whose values are as great as about 0.2 division, with a very fair degree of accuracy, both as regards amplitude and phase. Different determinations of harmonics of amplitudes as large as one division do not differ by more than a few per cent in amplitude nor more than a degree or two in the value of ψ. (The accuracy of reading of the fundamental ordinates is not greater than about 0.1 division.) The preceding assumes, however, that a sufficient number of harmonics have been included in the analysis. In the case of the curve of Example 3 as analyzed by the 12-point schedule, for instance, the effect of the thirteenth and fifteenth harmonics is distributed between the three highest harmonics included, and their values are different, both in amplitude and phase in analyses using different sets of ordinates.

In answer to the question as to how small harmonics in the above examples have been proved to exist, there seems to be reason to believe that, in some cases, the analysis has located with some degree of accuracy, harmonics of amplitude as small as 0.1 division which, considering that this is about the order of errors in reading the ordinates, points to a very satisfactory performance of the curve tracer.

EXAMPLE 6. PREDICTION OF PRESENCE OF HARMONICS FROM THE APPEARANCE OF THE CURVE

It is of interest to consider, in the case of distorted waves, how far one may predict from the appearance of the curves what important harmonics are present. Provided only one harmonic is present to a notable extent, its presence is manifested by a waviness of the curve, and the number of the crests and troughs per half wave of the fundamental will be equal to the order of the harmonic. When, however, more than one harmonic is important, it will not, in general, be possible to locate them all by counting the crests and troughs superposed on the fundamental.

As an example, we may take the curve of Example 3 (Curve A, Fig. 3). Fifteen maxima and minima (of very different amplitudes it is true) may be counted in each half wave of the curve. However, analysis has already shown that not only is the fifteenth harmonic prominent, but also the thirteenth, third, and fifth, to about an equal extent, while the amplitudes of the seventh, ninth, and eleventh are by no means negligible. It is interesting to study how these various harmonics combine in their effects to produce the observed distortion of the wave. In Fig. 3 is plotted in dashed lines the fundamental wave given by the analysis. In Fig. 4 the curve A shows the deviations of the distorted wave from the fundamental given by the analysis, as a function of the phase, referred to the arbitrary origin of the analysis. This origin lies about 1°.6 to the left of the zero of the fundamental. The dotted curves in Fig. 4 show graphically the amplitudes and phases of the third, fifth, thirteenth, and fifteenth harmonics given by the analysis. The plotting of these waves is an easy matter, since for those of the higher frequencies, little needs to be done except to indicate the position of the zero points and maxima and minima, the rest of the curve being drawn in free hand. The curve B defined by the little circles is the resultant of the waves of the third, fifth, thirteenth, and fifteenth harmonics. The period of the ripples lies somewhere between that of the thirteenth and fifteenth harmonics. The small deviations of the actual curve from this resultant curve may be shown to be

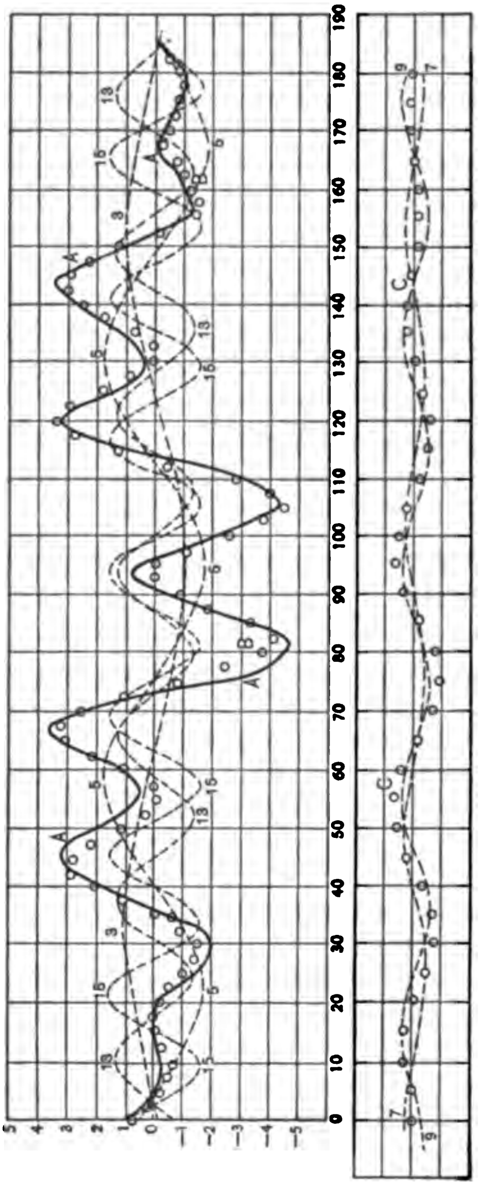

Fig. 4.—*Curves showing distorting effects of the various harmonics in electromotive force wave, curve A, Fig. 3.*

reduced practically to zero when the remaining harmonics are taken into consideration. These have been omitted for the sake of clearness, but the curves of the seventh and ninth harmonics, together with their resultant, C, are drawn in the lower part of the figure. If the ordinates of curve C are added to those of curve B the resulting curve agrees very closely with the actual curve A.

This example shows, therefore, that in many cases it is not possible to tell from the appearance of the curve what harmonics are present. In the present instance, from the number of ripples the presence of the fifteenth harmonic only could be predicted with certainty, while the almost equally important thirteenth and the still greater fifth harmonics would not be included. Naturally, however, the varying height of the different troughs and crests would lead one to suspect more than one harmonic.

EXAMPLE 7. BADLY DISTORTED CURVES—INFLUENCE OF CAPACITY AND INDUCTANCE

In the curves considered in the previous examples, the curves, although by no means closely approaching pure sine curves in character, are very far from showing the irregularities in wave form which often occur in circuits containing capacity. The curve B of Fig. 5 shows the current through a capacity of nine microfarads. The emf impressed on the condensers (and a resistance of 0.7 ohm joined in series for drawing the curve) is curve A of the same figure.

Analysis of the current curve by means of the 18-point schedule gives the following values of the amplitudes and phases of the components:

		Values reduced to emf.
$C_1 = 22.84$	$\psi_1 = -81^\circ.7$	
$C_3 = 2.28$	$\psi_3 = +38.3$	1.17
$C_5 = 7.22$	$\psi_5 = 30.5$	2.21
$C_7 = 11.48$	$\psi_7 = 8.0$	2.53
$C_9 = 1.51$	$\psi_9 = 10.8$	0.26
$C_{11} = 7.17$	$\psi_{11} = 27.9$	1.00
$C_{13} = 0.28$	$\psi_{13} = 13.0$	0.03
$C_{15} = 0.85$	$\psi_{15} = 16.8$	0.09
$C_{17} = 0.66$	$\psi_{17} = 1.3$	0.06

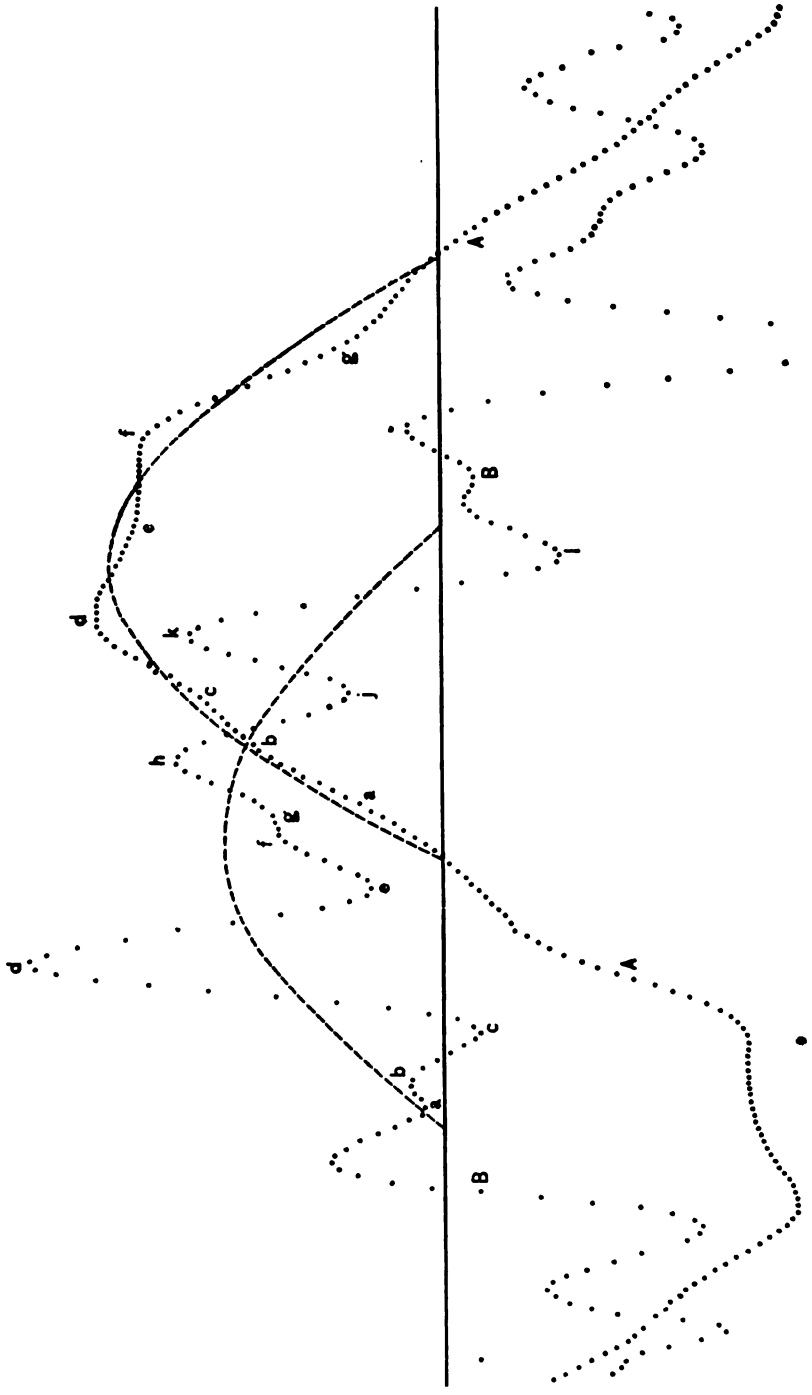

Fig. 5.—*Curve A, electromotive force wave impressed. Curve B, current in condenser circuit*

On calculating the deviations of this curve from the actual, using the scheme of calculation in Table 4 for this purpose, it was found that the departure is on the average not greater than about one division, an agreement which is to be regarded as satisfactory when the extreme steepness of the curve in some parts of its course is considered. Analysis of the emf wave gave

$$\begin{array}{ll}
C_1 = 35.01 & \psi_1 = -\ 2.1^\circ \\
C_3 = \ 0.99 & \psi_3 = +58.2 \\
C_5 = \ 1.90 & \psi_5 = \ 38.3 \\
C_7 = \ 1.93 & \psi_7 = \ 12.2 \\
C_9 = \ 0.09 & \psi_9 = \ 11.2 \\
C_{11} = \ 0.45 & \psi_{11} = \ 26.4 \\
C_{13} = \ 0.18 & \psi_{13} = \ 13.5 \\
C_{15} = \ 0.08 & \psi_{15} = \ 4.0 \\
C_{17} = \ 0.03 & \psi_{17} = \ 20.5
\end{array}$$

In a circuit containing capacity, but in which the resistance is negligible, the harmonics in the emf. wave are magnified in the current wave in proportion to the order of the harmonic. To test the accuracy of this relation in the case of the curves just given, the third column in the results of the analysis of the current curve given above, the column designated as "values reduced to emf.," was obtained by multiplying each harmonic in the current wave by the ratio of the fundamentals $\left(\frac{35.01}{22.84}\right)$ and dividing by the order of the harmonic in question. The general qualitative agreement of these calculated values with the harmonics of the emf wave is perhaps as good as could be expected when it is remembered that in addition to the 0.7 ohm the rest of the circuit was not of negligible resistance.

The same generator when run on an inductive load gave an emf. curve B, Fig. 1, which yielded on analysis

$$\begin{array}{llll}
C_1 = 33.96 & \psi_1 = -1.0^{\circ} \\
C_3 = 0.34 & \psi_3 = +60.6 \\
C_5 = 0.93 & \psi_5 = 35.9 \\
C_7 = 0.75 & \psi_7 = 50.8 \\
C_9 = 0.14 & \psi_9 = 1.0 \\
C_{11} = 1.50 & \psi_{11} = 16.5 \\
C_{13} = 0.27 & \psi_{13} = 4.7 \\
C_{15} = 0.08 & \psi_{15} = 20.7 \\
C_{17} = 0.09 & \psi_{17} = 18.0
\end{array}$$

The armature has 12 slots per cycle.

Not only is the shape of the curve very different from that given on a capacity load, curve A, Fig. 5, but, whereas in the latter case the third, fifth, and seventh harmonics were present to a marked degree, the eleventh harmonic is most prominent on inductive load. This gives a very striking illustration of the effects of armature reactions.

The current in the inductive circuit, curve A, Fig. 1, has already been analyzed and discussed in Example 1. The results show that the effect of inductance is to smooth out the harmonics in the emf. to an extent which is proportional to the order of the harmonic. For a more accurate experimental verification of this principle, the reader is referred to an article in this Bulletin.[8]

TABLE 11

Showing Relative Values of the Harmonics to Form the Crests and Troughs of the Curves in Example 7

CONDENSER CURRENT

Crest or trough	Harmonics				Sum	Observed deviation
	3	5	7	11		
a	1.0	−3.6	3.6	−3.6	− 2.6	− 2.3
b	1.6	−6.2	− 5.0	5.0	− 4.6	− 4.0
c	2.2	−6.0	−10.2	−2.2	−16.2	−15.2
d	0.7	6.5	11.0	6.9	25.1	24.8
e	−1.3	1.7	−10.4	−5.0	−15.0	−14.8
f	−2.2	−6.6	0.0	5.0	− 3.8	− 5.4
g	−2.0	−7.1	9.0	−3.5	− 3.6	− 4.1
h	−0.7	−0.7	5.0	2.7	6.3	6.4
j	1.2	7.1	−11.3	−5.0	− 8.0	− 7.3
k	2.2	−1.0	10.4	6.9	18.5	15.0
l	1.0	−6.4	− 4.8	−4.8	−15.0	−15.5

---

[8] This Bulletin, I, p. 140; 1904.

TABLE 11—Continued

CONDENSER ELECTROMOTIVE FORCE

Crest or trough	Harmonics			Sum	Observed deviation
	3	5	7		
a	−0.6	−1.4	0.4	−1.6	−2.2
b	−0.9	−0.6	1.1	−0.4	−0.7
c	−0.5	1.0	−1.3	−0.8	−1.5
d	0.7	0.7	1.8	3.2	3.2
e	0.6	−1.4	−1.9	−2.7	−2.2
f	−0.7	1.7	1.7	2.7	3.4
g	−1.0	−1.0	−1.9	−3.9	−4.4

INDUCTIVE ELECTROMOTIVE FORCE

Crest or trough	Harmonics				Sum	Observed deviation
	3	5	7	11		
a	−0.2	−0.5	0.5	−1.5	−1.7	−1.8
b	−0.3	−0.8	0.3	1.3	0.5	0.0
c	−0.4	0.2	−0.7	−1.3	−2.2	−2.4
d	0.0	0.9	0.6	1.4	2.9	2.3
e	0.2	−0.5	−0.3	−1.1	−1.7	−2.1
f	0.4	−0.9	−0.7	1.3	0.1	0.0
g	0.3	−0.5	0.0	−1.2	−1.4	−1.4
h	0.0	0.8	0.5	1.4	2.7	2.3
j	−0.3	0.3	−0.7	−1.4	−2.1	−2.4
k	−0.3	−0.7	0.0	1.4	0.4	0.0
l	−0.1	0.5	−0.7	−1.4	−1.7	−1.6

It is of interest, in the case of each of these curves, to see how the shape of the curve depends on the principal harmonics present. In each case the fundamental component, derived by the analysis, is plotted in the figure as a dashed sine curve. Table 11 shows to what harmonics each trough and crest is due. For purposes of identification, these have been lettered. In the table are given the values of the harmonic components at the points in question, as derived from a plot of the results of the analysis, together with their resultant (algebraic sum). For comparison there are appended the actual measured deviations of the curve from the fundamental given by the analysis (the dashed sine curve). No attempt was made to obtain an accurate comparison, the table being given for purposes of orientation only.

EXAMPLE 8. RESONANCE OF A PARTICULAR HARMONIC

It sometimes happens that the inductance and capacity are of such values as to give resonance for some particular harmonic of the emf. wave. The curve *A*, Fig. 6, is an emf. wave taken from the same machine as in Example 3. The thirteenth and fifteenth harmonics are appreciable, amounting to about 3.8 per cent and 4.6 per cent of the fundamental, respectively. In this particular case it was found that on joining a Siemens dynamometer in the circuit to measure the current through a small capacity, the current indicated by the dynamometer was much larger than was expected from the known approximate value of the capacity. On drawing the current curve, the wave form was found to be that of curve *B*; the higher harmonics are seen at a glance to be very prominent. Analysis gave the following results:

$C_1 = 1.57 \qquad \psi_1 = -88.1^\circ$
$C_3 = 0.51 \qquad \psi_3 = -0.1$
$C_5 = 0.23 \qquad \psi_5 = -7.0$
$C_7 = 1.21 \qquad \psi_7 = 32.6$
$C_9 = 0.48 \qquad \psi_9 = 9.8$
$C_{11} = 1.75 \qquad \psi_{11} = 21.7$
$C_{13} = 1.21 \qquad \psi_{13} = 14.6$
$C_{15} = 4.94 \qquad \psi_{15} = 3.1$
$C_{17} = 0.63 \qquad \psi_{17} = -3.3$

All the harmonics included in the analysis are appreciable, the seventh, eleventh, and thirteenth being of the same order of magnitude as the fundamental, while the fifteenth harmonic has an amplitude of more than three times that of the fundamental, the condition of resonance being most completely realized for this harmonic. In fact, if the components be plotted, it is found that the successive maxima and minima of the curve coincide almost exactly with those of the fifteenth harmonic, although the remaining component waves influence the actual values of these maxima and minima to an extent which varies according as they act in conjunction or opposition.

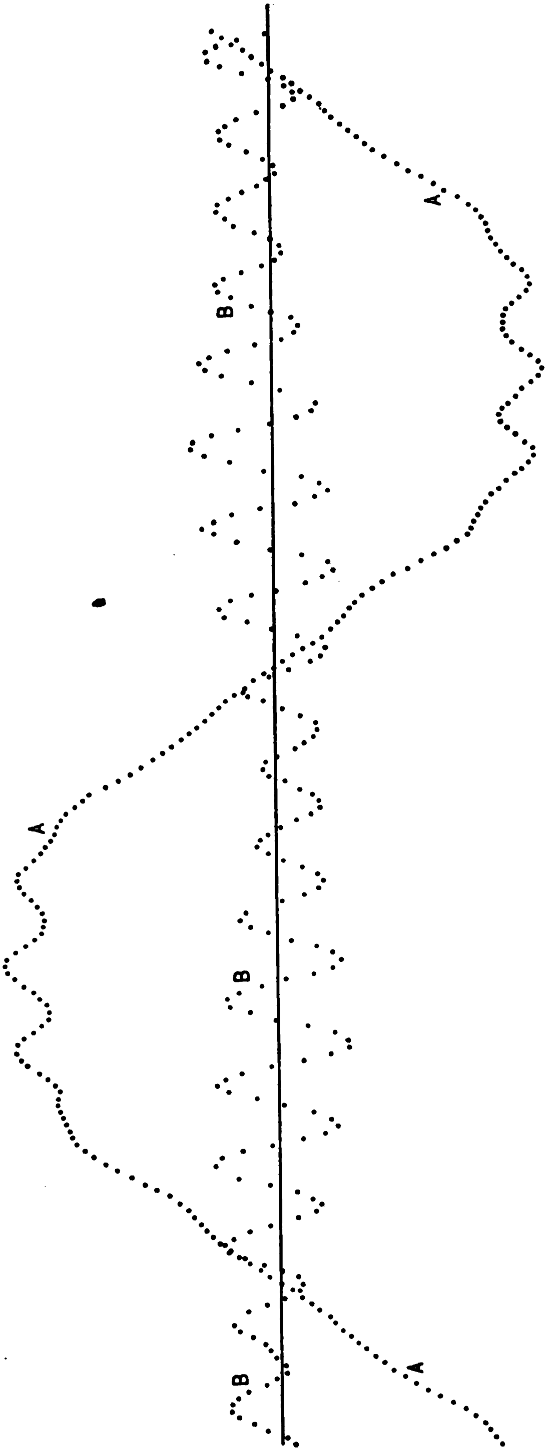

Fig. 6.—*Curve A, electromotive force wave. Curve B, current curve. Resonance of fifteenth harmonic*

The phases are referred to an origin taken arbitrarily at the extreme left-hand point of the current wave. The emf wave does not seem to have been drawn in the proper phase relation with the current curve.

In such cases as those in which resonance renders abnormally prominent some harmonic of an order higher than is included in the foregoing schedules of analysis, it is not difficult to derive a scheme of analysis for the single harmonic in question, according to the principles already laid down.

V. FURTHER APPLICATIONS

1. CALCULATION OF THE AVERAGE AND EFFECTIVE VALUES OF ELECTROMOTIVE FORCE AND CURRENT CURVES

It is customary to define the *average* value of an emf or current wave as the average ordinate of one loop of the curve (either positive or negative); since the positive and negative loops are alike the average of the ordinates throughout a complete period is zero. In the case of very distorted waves, as for instance, that of the condenser current, Fig. 5, it is difficult, if not impossible, to state where is the beginning of a loop. The usual custom of taking as the beginning of the loop the point where the curve passes through zero, evidently becomes inapplicable when the curve is constantly oscillating between positive and negative values. The average value of an emf. or current wave is consequently a quantity which depends on the choice of origin of phase differences, and it is difficult to define it in such a way as to include the customary rather special definition of this quantity. In what follows the average value of an emf. or current wave will be defined as the average ordinate of one-half wave, counting phase differences from the *zero of the fundamental* as origin. This definition does not give quite the same value as that found by taking as origin the point (in the case of only slightly distorted waves) where the curve crosses the axis, but the difference will, in general, be found small.

With this understanding, and writing for the equation of the wave

$$e = E_1 \sin \frac{2\pi}{T} t + E_3 \sin \left[3\left(\frac{2\pi}{T}\right)t - \beta_3\right] + \ . \ . \ .$$
$$+ E_n \sin \left[n\left(\frac{2\pi}{T}\right)t - \beta_n\right] + \ . \ . \ .$$

the average value ϵ is defined by the expression

$$\epsilon = \frac{2}{T}\Big[E_1 \int_0^{\frac{T}{2}} \sin \frac{2\pi}{T} t \, dt + E_3 \int_0^{\frac{T}{2}} \sin \left(3\frac{2\pi}{T} t - \beta_3\right) dt + \ldots$$
$$+ E_n \int_0^{\frac{T}{2}} \sin \left(n\frac{2\pi}{T} t - \beta_n\right) dt + \ldots \Big]$$

where T is the period of the fundamental.

We have, therefore, to evaluate the general integral

$$\int_0^{\frac{T}{2}} \sin \left(\frac{2\pi n}{T} t - \beta_n\right) dt$$

which is easily found to be equal to $\frac{T}{\pi n} \cos \beta_n$, so that the final expression for the average value is

$$\epsilon = \frac{2}{\pi} \Sigma \frac{E_n}{n} \cos \beta_n \tag{14}$$

where $$\beta_n = n(\psi_n - \psi_1)$$

and ψ_n has the same meaning as in equation (13).

The *root mean square* or *effective* value is involved in no such ambiguity as the *average* value, being entirely independent of what point is chosen as origin. Writing the equation of the curve in the form

$$e = E_1 \sin \left(\frac{2\pi}{T} t - \theta_1\right) + E_3 \sin \left(3\frac{2\pi}{T} t - \theta_3\right) + \ldots$$
$$+ E_n \sin \left(n\frac{2\pi}{T} t - \theta_n\right) + \ldots$$

we have for the square of the instantaneous value

$$e^2 = E_1^2 \sin^2 \left(\frac{2\pi}{T} t - \theta_1\right) + E_3^2 \sin^2 \left(3\frac{2\pi}{T} t - \theta_3\right) + \ldots$$
$$+ E_n^2 \sin^2 \left(n\frac{2\pi}{T} t - \theta_n\right) + \ldots$$
$$+ 2E_1E_n \sin \left(\frac{2\pi}{T} t - \theta_1\right) \sin \left(n\frac{2\pi}{T} t - \theta_n\right) + \ldots$$
$$+ 2E_3E_n \sin \left(3\frac{2\pi}{T} t - \theta_3\right) \sin \left(n\frac{2\pi}{T} t - \theta_n\right) + \ldots$$

and the square of the effective value will be $\mathbf{E}^2=\frac{1}{T}\int_0^T e^2dt.$ The integrals of the form $\int_0^T \sin\left(m\frac{2\pi}{T}t-\theta_m\right)\sin\left(n\frac{2\pi}{T}t-\theta_n\right)dt$ are easily seen to be each separately equal to zero, so that there remain only integrals of the general form $\int_0^T \sin^2\left(n\frac{2\pi}{T}t-\theta_n\right)dt$, which, using the relation $\int \sin^2 xdx=\frac{x}{2}-\frac{\sin x \cos x}{2}$, are found to give merely the term $\frac{T}{2}$ so that we have the simple expression

$$\mathbf{E}^2=\frac{1}{2}(E_1^2+E_3^2+ \ . \ . \ . \quad +E_n^2+ \ . \ . \ .) \tag{15}$$

2. CALCULATION OF THE AVERAGE POWER IN A CIRCUIT

The average power in a circuit is found by taking the average of the values of the instantaneous power (ei) through an entire period. This may, of course, be calculated by measuring a sufficient number of ordinates of the emf and current curves, and by forming the products of corresponding values of the ordinates of the two waves. The average power may, however, be much more readily and more accurately calculated from the results of an analysis of the current and emf waves. Writing as usual

$$e=E_1 \sin\left(\frac{2\pi}{T}t-\theta_1\right)+E_3 \sin\left(3\frac{2\pi}{T}t-\theta_3\right)+ \ . \ . \ .$$
$$+E_n \sin\left(n\frac{2\pi}{T}t-\theta_n\right)+ \ . \ . \ .$$

$$i=I_1 \sin\left(\frac{2\pi}{T}t-\delta_1\right)+I_3 \sin\left(3\frac{2\pi}{T}t-\delta_3\right)+ \ . \ . \ .$$
$$+I_n \sin\left(n\frac{2\pi}{T}t-\delta_n\right)+ \ . \ . \ .$$

the instantaneous power is given by

$$
\begin{aligned}
ei = {} & E_1I_1 \sin\left(\frac{2\pi}{T}t-\theta_1\right)\sin\left(\frac{2\pi}{T}t-\delta_1\right) \\
& + E_3I_3 \sin\left(3\frac{2\pi}{T}t-\theta_3\right)\sin\left(3\frac{2\pi}{T}t-\delta_3\right) + \ldots \\
& + E_1I_3 \sin\left(\frac{2\pi}{T}t-\theta_1\right)\sin\left(3\frac{2\pi}{T}t-\delta_3\right) + \ldots + \\
& E_1I_n \sin\left(\frac{2\pi}{T}t-\theta_1\right)\sin\left(n\frac{2\pi}{T}t-\delta_n\right) + \ldots . \\
& + E_3I_1 \sin\left(3\frac{2\pi}{T}t-\theta_3\right)\sin\left(\frac{2\pi}{T}t-\delta_1\right) \\
& + E_3I_5 \sin\left(3\frac{2\pi}{T}t-\theta_3\right)\sin\left(5\frac{2\pi}{T}t-\delta_5\right) + \ldots
\end{aligned}
$$

and the average power is found by performing the integration of this expression between the limits zero and T, and by then dividing the result by T. The integrals of the form $\int_0^T \sin\left(m\frac{2\pi}{T}t-\theta_m\right)\sin\left(n\frac{2\pi}{T}t-\delta_n\right)dt$ are all separately equal to zero. The remaining integrals are of the form

$$
\int_0^T \sin\left(n\frac{2\pi}{T}t-\theta_n\right)\sin\left(n\frac{2\pi}{T}t-\delta_n\right)dt =
$$

$$
\frac{1}{2}\int_0^T\left[\cos\left(\theta_n-\delta_n\right)-\cos\left\{2n\frac{2\pi}{T}t-\left(\theta_n+\delta_n\right)\right\}\right]dt
$$

which, since $\int_0^T \cos\left[2n\frac{2\pi}{T}t-\left(\theta_n+\delta_n\right)\right]dt = \text{zero}$ are seen to give the final expression for the average power

$$
\begin{aligned}
P &= \frac{1}{2}\left[E_1I_1\cos\left(\theta_1-\delta_1\right)+E_3I_3\cos\left(\theta_3-\delta_3\right)+\ldots+E_nI_n\cos\left(\theta_n-\delta_n\right)\right] \qquad (16) \\
&= \frac{1}{2}\left[E_1I_1\cos\varphi_1+E_3I_3\cos\varphi_3+\ \ldots\ +E_nI_n\cos\varphi_n+\ \ldots\ \right]
\end{aligned}
$$

where φ_n is the angle of phase difference between the harmonic emf. of n times the frequency of the fundamental and the current component of the same frequency. This equation expresses the well-known fact that on the average electromotive forces and currents of different frequencies add nothing to the power of a circuit.

The power factor of a circuit, in which the emf and current may have any wave form whatever, is defined as the ratio of the average power to the product of the effective emf. by the effective current. In the case of pure sine waves it is equal to the cosine of the phase difference between the emf. and the current; in the case of distorted waves, the power factor may be designated as the cosine of an angle, which we may call the *effective phase difference,* an angle which has no physical existence, but which is equal to the phase difference which would have to exist between two sine waves having, respectively, the same effective values as the emf. and current, and developing the same average power as the actual emf. and current.

We thus see that if the results of the analysis of the emf. and current curves in a circuit are at hand, it is an easy matter to calculate the average and effective values of the emf and current, the form factor, the average power, the power factor, and the effective phase difference between the emf. and the current. Of these quantities, some may be calculated from the curves, by measuring a sufficient number of ordinates, and forming the averages of their squares and products. The *average* values of emf. and current (and therefore their form factors) can not, however, be accurately found without having analyzed the curves (in the case of very distorted waves an analysis is absolutely essential), and all the above quantities may be found more accurately and more expeditiously from the analysis than from the laborious method of working from a large number of measured ordinates. Numerical examples of the use of formulas (14), (15), and (16) will be given below in Examples 9, 10, and 11.

3. DERIVATION OF THE EQUATIONS OF POWER CURVES

The equation of the curve showing the *instantaneous power* during the cycle follows without difficulty from the equations of the emf. and current curves.

Writing

$$e = E_1 \sin (pt - \theta_1) + E_3 \sin (3pt + \theta_3) + \dots \quad + E_n \sin (npt - \theta_n) + \dots$$

$$i = I_1 \sin (pt - \delta_1) + I_3 \sin (3pt - \delta_3) + \dots \quad + I_n \sin (npt - \delta_n) + \dots$$

we have for the power

$$
\begin{aligned}
ei = E_1I_1 \sin(pt-\theta_1)\sin(pt-\delta_1) &+ E_1I_n \sin(pt-\theta_1)\sin(npt-\delta_n) + \ldots, \\
&E_3I_1 \sin(3pt-\theta_3)\sin(pt-\delta_1) + \ldots \\
&+E_3I_n \sin(3pt-\theta_3)\sin(npt-\delta_n) + \ldots \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
&E_nI_1 \sin(npt-\theta_n)\ (pt-\delta_1) + \ldots \\
&+E_nI_n \sin(npt-\theta_n)\sin(npt-\delta_n) + \ldots
\end{aligned}
\tag{17}
$$

Using the relation $2 \sin x \sin y = \cos(x-y) - \cos(x+y)$ the equation (17) falls into the following

$$
\begin{aligned}
2ei = E_1I_1 \cos(\delta_1-\theta_1) &+ E_3I_3 \cos(\delta_3-\theta_3) + \ldots \\
&+ E_nI_n \cos(\delta_n-\theta_n) + \ldots \\
&+ \text{terms involving the cosines of even multiples of } pt.
\end{aligned}
$$

The first line of the preceding equation gives the average power, as has already been shown. The cosine terms are of the form $P_n \cos[2npt-\alpha_1]$, $Q_n \cos[2npt-\alpha_2]$ etc. These terms can be simplified by using the relation

$$
\begin{aligned}
M_1 \cos(x-\alpha_1) + M_2 \cos(x-\alpha_2) + M_3 \cos(x-\alpha_3) + \ldots \\
= N \sin(x-\gamma)
\end{aligned}
\tag{17a}
$$

where

$$
\begin{aligned}
N^2 = (M_1 \sin\alpha_1 + M_2 \sin\alpha_2 + M_3 \sin\alpha_3 + \ldots)^2 + (M_1 \cos\alpha_1 \\
+ M_2 \cos\alpha_2 + M_3 \cos\alpha_3 + \ldots)^2
\end{aligned}
$$

and

$$
\tan\gamma = \frac{-(M_1 \cos\alpha_1 + M_2 \cos\alpha_2 + M_3 \cos\alpha_3 + \ldots)}{(M_1 \sin\alpha_1 + M_2 \sin\alpha_2 + M_3 \sin\alpha_3 + \ldots)}
$$

The equation for the power then reads

$$
\begin{aligned}
2ei = 2P = E_1I_1 \cos(\delta_1-\theta_1) &+ E_3I_3 \cos(\delta_3-\theta_3) + \ldots \\
&+ E_nI_n \cos(\delta_n-\theta_n) + \ldots \\
&+ N_1 \sin(2pt-\gamma_1) + N_2 \sin(4pt-\gamma_2) \\
&+ N_3 \sin(6pt-\gamma_3) + \ldots
\end{aligned}
\tag{18}
$$

This procedure will be illustrated by Example 12, below. In those cases where the higher harmonics in both the current and emf. wave are not negligible, the number of terms which must be included in equation (17) becomes large, and the method becomes more laborious. In such a case it may often be easier to form the products of the ordinates used in the analysis of the emf and current curves, and carry through the analysis of the power curve using the schedules for the analysis of curves in which even harmonics are included. (See Appendix B.) Both methods are illustrated in Example 12, and are seen to give essentially the same equation, as should be the case.

4. RESOLUTION OF THE POWER CURVE INTO TWO COMPONENTS.

It is often of interest to resolve the power curve into two components, one representing the power lost in the circuit in such ways as in heating a resistance, in iron losses, or in dielectric losses, and a second showing the rate at which energy is alternately stored in and recovered from the magnetic field or the dielectric. The average value of the power *dissipated* is $EI \cos \phi$, where E and I are, respectively, the effective values of the emf and the current, and $\cos \phi$ is the power factor, the angle ϕ being in the case of sine waves the angle of phase difference between the emf. and the current.

In the case of sine waves it is mathematically the same, as far as the value of the average power is concerned, whether we resolve the emf. into two components $E \cos \phi$ and $E \sin \phi$, respectively in phase and in quadrature with the current, and take the products of these components with the current, or whether we consider the components of the power to be the result of taking the products of the emf. with the two currents $I \cos \phi$ and $I \sin \phi$, found by resolving the current along the emf. vector and at right angles to it, respectively.

Thus, it is customary to speak of the *power* and *wattless* components of the current as well as of the corresponding quantities for the emf. Logically, however, it does not seem to be correct to speak of a wattless component of the current, since in the power loss I^2r, not only the "power" component $I \cos \phi$, but also the component $I \sin \phi$ of the current enters. Further, it is easy to show that of these two methods of resolution only that where the emf. is split up into power and wattless components gives a correct picture of the facts of the case. However, since it is very often convenient to make use of the conceptions of the "power" and "wattless" components of the current, as defined above (as, for example, in the usual treatment of the theory of the magnetizing current of a transformer), both methods will be treated below, after we have first considered wherein the two methods of treatment differ.

Assuming the emf and current to vary according to a simple sine law, we may put for the instantaneous values of emf and current

$$\begin{aligned} e &= E \sin pt \\ i &= I \sin (pt - \phi) \end{aligned} \tag{18a}$$

and the instantaneous value of the power is given by

$$ei = \frac{1}{2} EI \left[\cos \phi - \cos (2pt - \phi)\right] \tag{19}$$

The average value of the second term is zero; the first term gives the usual expression for the average value of the power, i. e., the average value of the power *dissipated.*

Let us consider the case of an inductive circuit; entirely similar relations follow if capacity is also assumed to be present. Resolving the emf. into two components, e_1 and e_2, respectively in phase with the current, and 90° ahead of it in phase, we may write

$$\begin{aligned} e_1 &= E \cos \phi \sin (pt - \phi) \\ e_2 &= E \sin \phi \cos (pt - \phi) \end{aligned} \tag{20}$$

and thence,

$$\begin{aligned} e_1 i &= \frac{1}{2} EI \cos \phi \left[1 - \cos (2pt - 2\phi)\right] \\ e_2 i &= \frac{1}{2} EI \sin \phi \sin (2pt - 2\phi) \end{aligned} \tag{21}$$

The sum of these two component power curves gives the same expression for the total power as in equation (19).

If we resolve the current into two components, i_1 and i_2, respectively in phase with the emf and 90° behind it in phase, we find

$$\begin{aligned} i_1 &= I \cos \phi \sin pt \\ i_2 &= -I \sin \phi \cos pt \end{aligned} \tag{22}$$

and, accordingly

$$\begin{aligned} ei_1 &= \frac{1}{2}EI\cos\phi[1-\cos 2pt] \\ ei_2 &= \frac{1}{2}EI\sin\phi\sin 2pt \end{aligned} \tag{23}$$

The sum of these two components gives the same equation (19) for the total power as before.

The power equation for an inductive circuit may be written

$$ei = Ri^2 + \frac{d}{dt}\left(\frac{1}{2}Li^2\right) \tag{24}$$

the first term giving the rate at which energy is being dissipated, the second term the rate at which the kinetic energy of the current is being changed.

Substituting the value of i from (18a), we find

$$\begin{aligned} Ri^2 &= \frac{1}{2}I^2R\,[1-\cos(2pt-2\phi)] \\ &= \frac{1}{2}EI\cos\phi[1-\cos(2pt-2\phi)] \end{aligned} \tag{25}$$

since the equation $I = \frac{E}{R}\cos\phi$ exists between the maximum values of current and emf.

The second term gives

$$\begin{aligned} \frac{1}{2}\frac{d}{dt}(Li^2) &= \frac{1}{2}LpI^2\sin(2pt-2\phi) \\ &= \frac{1}{2}EI\sin\phi\sin(2pt-2\phi) \end{aligned} \tag{26}$$

since $LpI = E\sin\phi$.

The two component curves of instantaneous power in equation (21), found by resolving the emf. into an in-phase component and a quadrature component, with respect to the current, are thus seen to represent correctly at every instant, the values of the power expended in Joule heat and the power stored in the magnetic field, equations (25) and (26).

If we now substitute the relation $i = i_1 + i_2$ in (24), the power equation may be written

$$ei = R(i_1^2 + 2i_1 i_2 + i_2^2) + L\left(i_1\frac{di_1}{dt} + i_2\frac{di_2}{dt} + i_1\frac{di_2}{dt} + i_2\frac{di_1}{dt}\right) \tag{27}$$

and, using the values of i_1 and i_2 from (22), it is easy to show that the two components of the power ei_1 and ei_2 in equation (23) are given by the two sums of terms $R(i_1^2 + i_2^2) + L\left(i_1\frac{di_2}{dt} + i_2\frac{di_1}{dt}\right)$ and $2Ri_1 i_2 + L\left(i_1\frac{di_1}{dt} + i_2\frac{di_2}{dt}\right)$ respectively, which together make up (27).

Remembering that the phases of $\frac{di_1}{dt}$ and $\frac{di_2}{dt}$ are 90° ahead of i_1 and i_2, respectively, it appears that the first series of terms consists of products of pairs of in-phase quantities, while the second series consists of products of quantities in quadrature with one another. The separation of those terms in the equation of the power which, on the average, contribute to the average power, from those terms whose average value taken over the cycle is zero, is therefore correctly carried out, but this resolution of the current must nevertheless be regarded as artificial rather than as representing the actual physical relations.

Passing to the consideration of nonharmonic waves, let us write, as before,

$$\begin{aligned} e &= E_1 \sin(pt - \theta_1) + E_3 \sin(3pt - \theta_3) + E_5 \sin(5pt - \theta_5) + \ldots \\ i &= I_1 \sin(pt - \delta_1) + I_3 \sin(3pt - \delta_3) + I_5 \sin(5pt - \delta_5) + \ldots \end{aligned} \tag{28}$$

Remembering that the product of any harmonic of the emf wave by any harmonic of different frequency in the current wave contributes nothing to the average value of the power taken over the cycle, it is logical to write for the power and wattless components of the emf the following equations of definition

$$\begin{aligned} e_1 &= E_1 \cos(\delta_1 - \theta_1) \sin(pt - \delta_1) + E_3 \cos(\delta_3 - \theta_3) \sin(3pt - \delta_3) + \ldots \\ e_2 &= E_1 \sin(\delta_1 - \theta_1) \cos(pt - \delta_1) + E_3 \sin(\delta_3 - \theta_3) \cos(3pt - \delta_3) + \ldots \end{aligned} \tag{29}$$

For the components of the current in phase and in quadrature with the emf, we have the similar equations

$$\begin{aligned} i_1 &= I_1 \cos(\delta_1 - \theta_1) \sin(pt - \theta_1) + I_3 \cos(\delta_3 - \theta_3) \sin(3pt - \theta_3) + \ldots \\ & \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (30) \\ -i_2 &= I_1 \sin(\delta_1 - \theta_1) \cos(pt - \theta_1) + I_3 \sin(\delta_3 - \theta_3) \cos(3pt - \theta_3) + \ldots \end{aligned}$$

If the harmonics E_1, E_3, . . . and I_1, I_3, . . . of the emf. and current are already known from previous analysis of the curves, it is evidently a very simple matter to write down the equations of these component emfs and currents, and these may be used to derive the equations of the component power curves as will be shown below. If, however, the form of the curves given in these equations is of interest, it is necessary to plot these equations, which is a laborious undertaking. In case the harmonics are mostly all small, or negligible, the matter is simplified, since the harmonic waves may be drawn accurately enough without calculation. For this the zero points and the positions of the maxima and minima are plotted and the rest of the curves drawn in free hand. The resultant curve of these harmonic waves may then be determined graphically, and its ordinates show the deviation of the actual curve from the simple sine wave of the fundamental. The latter may be plotted carefully, and corrected by means of the curve of deviations, to obtain a sufficiently accurate representation of the actual curve.

5. DERIVATION OF THE EQUATIONS OF COMPONENT POWER CURVES

The equations for $e_1 i$ and $e_2 i$ are found by multiplying the expressions (29) by the equation (28) for i. In the case of the component $e_1 i$ there will also be, in addition to the series of constant terms which express the average power (see equation (16)), a series of terms of the form $P \sin(mpt - \delta_m) \,.\, \sin(npt - \delta_n)$, which may be resolved by the relation $2 \sin(mpt - \delta_m) \sin(npt - \delta_n) = \cos[(m-n)pt - (\delta_m - \delta_n)] - \cos[(m+n)pt - (\delta_m + \delta_n)]$, and finally all the terms involving each frequency are to be collected into a single term involving the sine of the same frequency, by means of equations given already.

For the component $e_3 i$ we have terms of the form $Q \sin (mpt - \delta_m) \cos (npt - \delta_n)$, which may be resolved by the relation $2 \sin (mpt - \delta_m) \cos (npt - \delta_n) = \sin [(m+n)pt - (\delta_m + \delta_n)] - \sin [(m-n)pt - (\delta_m - \delta_n)]$, and then all the terms of the same frequency may be collected by means of the following transformation equations:

$$M_1 \sin (2npt - \alpha_1) + M_2 \sin (2npt - \alpha_2) + M_3 \sin (2npt - \alpha_3) + \ldots = N \sin (2npt - \gamma) \tag{31}$$

where

$$\begin{aligned} N^2 &= [M_1 \sin \alpha_1 + M_2 \sin \alpha_2 + M_3 \sin \alpha_3 + \ldots]^2 \\ &\quad + [M_1 \cos \alpha_1 + M_2 \cos \alpha_2 + M_3 \cos \alpha_3 + \ldots]^2 \\ \tan \gamma &= \frac{M_1 \sin \alpha_1 + M_2 \sin \alpha_2 + M_3 \sin \alpha_3 + \ldots}{M_1 \cos \alpha_1 + M_2 \cos \alpha_2 + M_3 \cos \alpha_3 + \ldots} \end{aligned} \tag{32}$$

The problem of finding the equations of the curves for ei_1 and ei_2 presents nothing essentially different from the foregoing considerations.

The details of these calculations will be clearer from a consideration of Examples 13*a* and 13*b*, in which are illustrated all the steps involved in the calculation of the equations of the curves of the power components.

The amount of labor necessary for the calculations rapidly increases with the number of harmonics present in the waves of emf and current, and if it were not for the amount of work necessary to calculate ordinates from the curves of the emf. or current components, it would be easier to actually carry through the analysis of the curves from a set of calculated ordinates as is done in Example 12 to obtain the equation of the total power curve.

VI. EXAMPLES ILLUSTRATING THE PRECEDING SECTION

EXAMPLE 9. CALCULATION OF THE AVERAGE VALUES OF CURRENT AND EMF. WAVES, FORMULA 14

To illustrate the formulas, we will consider the waves of emf. and current shown in Fig. 3, curves A and B. The details of the calculation of the average values are shown in Table 12. In the first column is given the order of the harmonic; in the second, the corresponding amplitudes found by analysis; in the third, the values of the phase angles ψ_n, as derived by analysis (Example 3). From these are calculated the values of $(\psi_n - \psi_1)$, and in column 5 the values of $\beta_n = n(\psi_n - \psi_1)$. Columns 6 and 7 give cos β_n and $\frac{E_n}{n}$, and in the last column appear the products $\frac{E_n}{n}$ cos β_n.

TABLE 12

Calculation of the Average Values of Current and Electromotive Force Waves

ELECTROMOTIVE FORCE

	E_n	ϕ_n	$\phi_n - \phi_1$	β_n	Cos β_n	$\frac{E_n}{n}$	Products
1	33.217	1°.6	0	0	1.0000	33.217	33.217
3	0.970	2.1	0°5	1°5	0.9997	0.323	0.323
5	1.702	41.7	40.1	200.5	−0.9367	0.340	− 0.319
7	0.218	38.3	36.7	256.9	−0.2267	0.031	− 0.007
9	0.355	2.2	0.6	5.4	0.9956	0.039	0.039
11	0.205	19.3	17.7	194.7	−0.9673	0.019	− 0.018
13	1.251	3.8	2.2	28.6	0.8780	0.096	0.084
15	1.528	15.7	14.1	211.5	−0.8526	0.102	− 0.087
17	0.159	3.0	1.4	23.8	0.9150	0.009	0.008
							33.671
			$33.240 \times \frac{2}{\pi} = 21.16$				− .431
			Average value of emf.			Sum	33.240

CURRENT

	I_n	ϕ_n	$\phi_n - \phi_1$	β_n	Cos β_n	$\frac{I_n}{n}$	Products
1	29.627	66°.9	0	0	1.0000	29.627	29.627
3	3.866	27.8	−39.1	−117.3	−0.4586	1.289	− 0.592
5	0.459	26.2	−40.7	−203.5	−0.9171	0.092	− 0.084
7	0.211	15.3	−51.6	−361.2	0.9998	0.030	0.030
9	0.155	11.6	−55.3	−497.7	−0.7396	0.017	− 0.013
11	0.163	15.4	−51.5	−566.5	−0.8949	0.015	− 0.014
13	0.214	9.9	−57.0	−741.0	0.9336	0.016	0.015
15	0.188	15.3	−51.6	−774.0	0.5878	0.013	0.008
17	0.052	18.1	−48.8	−829.6	−0.3355	0.003	− 0.001
							29.680
			$28.976 \times \frac{2}{\pi} = 18.45$				− .704
			Average value of current.			Sum	28.976

The sum of these latter, multiplied by $\frac{2}{\pi}$, gives the average ordinate of the emf wave as 21.16.

The second half of the table relates to the current wave, and the preceding explanation will make this clear. The average ordinate of the current was found to be 18.45.

As a check on these calculations the average values were also determined by actually measuring and summing the ordinates of each dot (phase difference of 2°) for half a cycle, taking as the origin the point where the curve crosses the axis. The values found were 21.29 for the emf and 18.60 for the current. The differences between these values and those found from the results of analysis of the curves are probably to be explained by the fact that only one-half of the wave was measured, while the analyses rest upon the average ordinates of a whole wave.

Similar calculations were made for the condenser current and emf. (curves B and A, Fig. 5), which have already been analyzed in Example 7. The condenser current is so irregular, crossing the axis so often, that one has to depend on the analysis to tell where the origin of phase should be taken to agree with our definition on page 608. The results of the two methods are given below.

	Calculated	Measured ordinates
Average emf	21.86	21.84
Average current	13.88	13.56

The labor of measuring all these ordinates and taking their sum is, of course, vastly greater than that of calculating the average value from the results of the curve analysis.

EXAMPLE 10. CALCULATION OF THE EFFECTIVE VALUES OF EMF. AND CURRENT, FORMULA 15

The same curves were treated as in the preceding example. Details of the calculation are given in Table 13.

TABLE 13

Calculation of the Effective Values of Current and Electromotive Force Waves

	Transformer Circuit				Condenser Circuit			
n	E_n	E_n^2	I_n	I_n^2	E_n	E_n^2	I_n	I_n^2
1	33.217	1,103.36	29.627	877.76	35.01	1,225.70	22.84	521.67
3	0.970	.94	3.866	14.95	0.99	0.98	2.28	5.20
5	1.702	2.90	0.459	0.21	1.90	3.61	7.22	52.13
7	0.218	.05	0.211	0.04	1.93	3.72	11.48	131.79
9	0.355	.13	0.155	0.02	0.09	0.01	1.51	2.28
11	0.205	.04	0.163	0.03	0.45	0.20	7.17	51.41
13	1.251	1.56	0.214	0.05	0.18	0.03	0.28	0.08
15	1.528	2.34	0.188	0.04	0.08	0.01	0.85	0.72
17	0.159	.03	0.052	0.00	0.03	0.00	0.66	0.44
		Sum 1,111.35		Sum 893.10		Sum 1,234.26		Sum 765.72
		Sum ÷ 2 = 555.68		Sum ÷ 2 = 446.55		Sum ÷ 2 = 617.13		Sum ÷ 2 = 382.86
Effective value		*23.57*		*21.13*		*24.84*		*19.56*
Value found from measured ordinates		*23.70*		*21.86*		*24.85*		*18.97*

In the first column is given the order of the harmonic, in the second the amplitudes of the various harmonics, as found by the analysis (Examples 3 and 7), and in the third column the squares of the amplitudes. Half the sum of the squares gives the square of the effective value.

As a check on these calculations, the effective values were also calculated by averaging the squares of the ordinates, already measured for calculating the average values in the previous example. The results thus found are also given in the table, and it will be seen that the agreement is satisfactory when it is considered that ordinates were measured for only one-half wave. In the case of the condenser current the changes of the current are so abrupt that the measured ordinates are apparently not close enough together to give a very accurate value.

For completeness the form factors of these curves are appended, as found both by calculation from the results of the analyses and as obtained from the measured ordinates.

Method	Transformer		Condenser	
	Emf	Current	Emf	Current
Analysis	1.114	1.145	1.137	1.409
Measured ordinates	1.113	1.1425	1.137	1.399

EXAMPLE 11. CALCULATION OF THE AVERAGE POWER, POWER FACTOR, AND EFFECTIVE PHASE DIFFERENCE, FORMULA 16

The same curves are considered here as in the preceding examples. In the first column of Table 14 is given the order of the harmonics. The second and third columns contain the amplitudes of the harmonics of the emf, and current, respectively, curves *A* and *B*, Fig. 3, while in the fourth and fifth appear the corresponding phase angles θ_n and δ_n, found by analysis. In column 6 are the calculated values of $(\delta_n - \theta_n)$, and in column 7 the cosines of these angles. The eighth and ninth columns give the products of the amplitudes and the power $E_n I_n \cos(\delta_n - \theta_n)$. The sum of these latter values, divided by 2, is the average power. The power factor is given by the quotient of this calculated value

TABLE 14

Calculation of the Average Power from the Results of the Analyses of Current and Emf. Waves

n	E_n	I_n	θ_n	δ_n	$\delta_n-\theta_n$	$\cos(\delta_n-\theta_n)$	E_nI_n	Products
			°	°	°			
1	33.217	29.627	1.6	66.9	65.3	0.4179	984.12	411.24
3	0.970	3.866	6.3	83.5	77.2	0.2215	3.75	0.83
5	1.702	0.459	208.8	131.0	− 77.8	0.2113	0.78	0.17
7	0.218	0.211	268.1	107.1	−161.0	−0.9455	0.05	− 0.04
9	0.355	0.155	20.1	104.6	84.5	0.0958	0.06	0.00
11	0.205	0.163	211.8	169.7	− 42.1	0.7420	0.03	0.02
13	1.251	0.214	49.3	129.1	79.8	0.1771	0.27	0.05
15	1.528	0.188	235.6	229.1	− 6.5	0.9936	0.29	0.29
17	0.159	0.052	51.1	308.0	256.9	−0.2250	0.01	− 0.00
							Sum	412.56
							Average power	*206.28*

Effective emf............ 23.57

Effective current........ 21.13

Power factor = 206.28 + (23.57 × 21.13) = *0.4142* = cos *65°5* of the average power by the product of the effective values of current and emf. found in the preceding example. The value found is 0.4142, which corresponds to an effective phase difference of 65°.5, a value not very different from the phase difference of 65°.3 existing between the fundamentals of current and emf.

The average power calculated directly from the measured ordinates of the emf and current waves is 212.7, which gives a power factor of 0.4223, corresponding to an effective phase difference of 65°.0.

Similar calculations were also made for the case of the condenser circuit considered in the preceding examples. As calculated from the equations of the curves of emf and current (see Example 7) the average power is 89.37, indicating a power factor of 0.1839 and an effective phase difference of 79°.4.

The scale of the emf curve, Fig. 5, was 20 divisions = 82 volts, while for the current 20 divisions = 0.71 ampere. The calculated values of the effective emf and current, expressed in divisions in Table 13, were, respectively, 101.7 volts and 0.637 ampere. The average power is therefore $89.37 \times 0.0355 \times 4.1$ or 13.03 watts, which corresponds to an effective resistance of $\frac{13.03}{(0.637)^2}$ or 27.0 ohms. This includes the equivalent resistance which represents the absorption of the condenser, as well as the actual resistance in series with the condenser. The capacity was about 9 mf.

By direct calculation from the ordinates of the emf and current curves the average power comes out as 79.57, which corresponds to a power factor of 0.1688 = cos 80°.3. Reducing to watts we have 11.58 watts, which indicates an effective resistance of 25.6 ohms.

The difference between the results by the two methods of calculation was explained when, on closer examination of the curves, it was noticed that the corresponding points of the current and emf. curves, used in the analyses, do not have exactly the same phase, but were given a displacement in the drawing of the curve of about 0.4 the phase difference of successive points, or 0°.8 in phase, and in such a direction as to make the phase difference found by analysis (on the assumption that corresponding ordinates have exactly the same phase) come out too small. Applying this correction the difference between the results by the two methods almost disappears. Attention is thus called to a source of error which must be guarded against if the results of the analyses are to be applied to the calculation of power factor.

EXAMPLE 12. DERIVATION OF THE EQUATION OF A POWER CURVE

In this example will be treated the derivation of the curve of instantaneous power for the emf and current curves, Fig. 3, already investigated in the previous examples. These are the curves of the magnetizing current in a transformer, at such a frequency that the magnetic induction was about double the normal value, together with the impressed emf causing this current to flow.

The problem will here be treated by two methods, (*a*) calculation from the results of the analysis of the emf and current waves, and (*b*) direct analysis, using as fundamental ordinates the products of the ordinates used in the analysis of the waves of emf and current.

(*a*) **First Method.**—The author's experience has led to the arrangement of the calculation exemplified in Table 15.

Columns 2 to 5 give the amplitudes and phase angles found in the analyses (Example 3) and the remainder of the first part of the table contains the separate products of the harmonic amplitudes of the current and emf, taken two at a time; thus the product of the ninth harmonic of the emf by the eleventh harmonic of the current appears in the column headed E_9 and in the row in which appears 11. It will be noticed that a good many of these products are, relatively, negligibly small, except in such cases as very high precision is desired. The labor of calculation may, therefore, in a good many cases be materially lessened by the omission of those terms which are of small importance.

In the second part of the table is illustrated the calculation of the amplitude and phase of one of the harmonics of the power curve—that harmonic which has a frequency of sixteen times the frequency of the fundamental of the current and emf.

In the third column are given those products E_mI_n, given in the first part of the table, for which the sum of the orders m and n of the harmonics is equal to the order of the desired harmonic; in this case 16. In the fourth column is given the sum of the phase angles, δ_n and θ_m of the current and emf harmonics, for

TABLE 15

Details of the Calculation of the Equation of a Power Curve from the Results of the Analysis of the Emf. and Current Curves

n	E_m	I_n	θ_m	δ_n	Products involving—								
					E_1	E_3	E_5	E_7	E_9	E_{11}	E_{13}	E_{15}	E_{17}
1	33.217	29.627	1°6	66°9	984.12	28.74	50.43	6.46	10.51	6.07	37.06	45.27	4.71
3	0.970	3.866	6.3	83.5	128.42	3.75	6.58	0.84	1.37	0.79	4.83	5.91	0.61
5	1.702	0.459	208.8	131.0	15.25	0.45	0.78	0.10	0.16	0.09	0.58	0.70	0.07
7	0.218	0.211	268.1	107.1	7.01	0.20	0.36	0.05	0.08	0.04	0.26	0.32	0.03
9	0.355	0.155	20.1	104.6	5.15	0.15	0.26	0.03	0.06	0.03	0.19	0.24	0.02
11	0.205	0.163	211.8	169.7	5.41	0.16	0.28	0.04	0.07	0.03	0.20	0.25	0.03
13	1.251	0.214	49.3	129.1	7.11	0.21	0.36	0.05	0.08	0.04	0.27	0.33	0.03
15	1.528	0.188	235.6	229.1	6.24	0.18	0.32	0.04	0.07	0.04	0.24	0.29	0.03
17	0.159	0.052	51.1	308.0	1.73	0.05	0.09	0.01	0.02	0.01	0.06	0.08	0.01

CALCULATION OF TERM IN 16 *pt.*

m	n	$M=E_mI_n$	Phase Angle α		$\sin\alpha$	$\cos\alpha$	$M\sin\alpha$	$M\cos\alpha$
			$\delta_n+\theta_m$	$\pm(\delta_n-\theta_m)$				
1	15	− 6.24	230°7		−0.7738	−0.6334	4.83	3.96
1	17	1.73		306°4	−0.8049	0.5934	− 1.40	1.03
3	13	− 0.21	135.4		0.7022	−0.7120	− 0.15	− 0.15
5	11	− 0.28	378.5		0.3173	0.9483	− 0.09	− 0.27
7	9	− 0.03	372.7		0.2198	0.9755	− 0.01	− 0.03
9	7	− 0.08	127.2		0.7965	−0.6046	− 0.06	0.05
11	5	− 0.09	342.8		−0.2940	0.9553	0.03	− 0.09
13	3	− 4.83	132.8		0.7337	−0.6794	− 3.54	3.28
15	1	−45.27	302.5		−0.8434	0.5373	38.18	−24.32
17	1	4.71		− 15.8	−0.2723	0.9622	− 1.28	4.52
						Sums	36.51	−12.02

$$N=\sqrt{36.51^2+12.02^2}=38.38$$

$$\tan\gamma=\frac{12.02}{36.51}\qquad \gamma=18°2$$

those cases in which the sum of the orders of the harmonics of emf and current is to be taken. Similarly, the fifth column contains the values of the differences of the phase angles of the harmonics of the current and emf corresponding to those cases where the differences of the indices m and n is equal to 16.

From the formula

$$2 \sin (mpt-\theta_m) \sin (npt-\delta_n) = \cos [(n-m)pt-(\delta_n-\theta_m)] \\ -\cos [(n+m)pt-(\delta_n+\theta_m)]$$

we see that the products E_mI_n, taken from the first part of the table, are to be given the positive or negative sign, according as the difference of n and m has to be taken to get 16, or the sum. Thus, in the first term $(n+m)=15+1$, and the negative sign is given to the product $E_1I_{15}=6.24$; in the second term $(n-m)=17-1$ and the product $E_1I_{17}=1.73$ is to be given the positive sign. With regard to the phases, we take the sum $(\delta_n+\theta_m)$ when $(m+n)=16$, and if $(n-m)=16$ the phase is $(\delta_n-\theta_m)$; if $(m-n)=16$, then $(\theta_m-\delta_n)$ is to be taken, hence the heading of the fifth column is given the double sign, with the understanding that the sign is to be taken as positive or negative according as n is greater or less than m.

In the sixth and seventh columns are given the sines and cosines of the phase angle, as just defined, and in the eighth and ninth columns the product of these functions with the corresponding values of E_mI_n. The derivation of the resultant amplitude of the harmonic from these quantities $M \sin \alpha$ and $M \cos \alpha$ is clearly indicated in the table, and is in accordance with equation (17*a*). The term in $16pt$ as thus found is $38.4 \sin (16pt-18°2)$.

Proceeding in this manner for each harmonic, the complete equation, including terms in $18pt$, is

$$\begin{aligned} 2P=2ei=412.56&+873.9 \sin (2pt-157°.6)+132.3 \sin (4pt-148°.3) \\ &+38.5 \sin (6pt-2°.6)+0.9 \sin (8pt-155°.2) \\ &+13.7 \sin (10pt-155°.0) \\ &+30.1 \sin (12pt-271°.9)+43.7 \sin (14pt-141°.2) \\ &+38.4 \sin (16pt-18°.2)+3.26 \sin (18pt-67°.1) \end{aligned}$$

The data in the Table 15 suffices to allow the equation to be extended to include terms in $34pt$. It is evident, however, from an inspection of the minuteness of the products E_mI_n, which would be used in calculating these higher terms, that all terms above that in $18pt$ must be practically negligible.

(*b*) **Second Method—Determination of the Equation of the Power Curve by Direct Analysis.**—For this purpose, the products were taken of the fundamental ordinates of the emf. curve, used in the analysis, by the corresponding ordinates which formed the basis of the analysis of the current curve. For convenience in plotting, these products were divided by 20 and were then used as fundamental ordinates in an analysis according to Schedule 3 in Appendix B. This schedule is for the analysis of a curve in which even harmonics and a constant term are included. Since 18 fundamental ordinates are required, the analysis gives, in addition to the constant term, the harmonics up to and including the *cosine* term of nine times the frequency of the fundamental. The term in the *sine* of nine times the frequency of the fundamental requires that a second set of ordinates lying halfway between those of the first set be measured, but the amplitude and phase of this term follow then immediately without further calculation.

The products of the emf. and current ordinates, used in this analysis, are spaced 10° apart in terms of the phase of the fundamental frequency of the emf and current, but since the fundamental of the power curve has twice the frequency of the fundamental of emf. and current, these 18 ordinates extend over the complete cycle of the power curve, and, therefore, fulfill the required conditions of the above scheme of analysis.

The detailed analysis of this power curve appears in Table 16 and illustrates the use of the Schedule 3, Appendix B. The work differs only in minor particulars from that in the case of the analysis of emf. and current curves in the Examples 1, 2, and 3.

The equation found by analysis is compared in Table 17 with that found by the first method of calculation, the amplitudes in this case having been divided by 20 to reduce to the same scale as that used in the analysis. The first column gives the frequency of the harmonic in terms of that of the fundamental of the emf. and current waves. The second and fourth columns give the amplitudes and phases found by the first method, the third and fifth the same quantities as given by the analysis.

The two curves are practically the same, as they should be, since they depend on the same data, namely, the results of the analysis of the emf. and current curves, or, what is the same

Analysis c

	Ordinates		s	d		1 and 8			
						+	−	+	-
0	− 0.15		− 0.15	− 0.15					
1	− 6.65	10.1	+ 3.45	−16.75	sin 20°		5.729		3.
2	−11.55	17.55	6.0	−29.1	sin 40°		10.092		18.
3	−12.0	27.05	15.05	−39.05	sin 60°		33.818		28.
4	−12.0	32.9	20.9	−44.9	sin 80°		37.029		44.
5	− 6.3	31.3	25.0	−37.6			− 86.668		−95.
6	+ 0.2	33.0	33.2	−32.8			− 95.038		
7	8.0	23.7	31.7	−15.7			−181.706		8.
8	10.7	21.55	32.25	−10.85		$A_1=$	−20.190	$A_8=$	0.
9	18.3		18.3	+18.3					

		1 and 8			
$\Sigma_0 = -0.15+33.2 = 33.05$		+	−	+	
$\Sigma_1 = 28.45+31.7 = 60.15$	sin 10°	3.629			4
$\Sigma_2 = 26.9+32.25 = 59.15$	sin 30°		16.600	7.525	
$\Sigma_3 = 15.05+18.3 = 33.35$	sin 50°	4.596			24
	sin 70°		30.305	3.242	
δ_0 92.20	sin 90°		0.150		18
δ_1 93.50		8.225	47.055	10.767	46
			−38.830		−36
$\Delta_1 = -32.45+37.6 = 5.15$			−74.997		− 2
$\Delta_2 = -39.95+44.9 = 4.95$		$B_1=$	− 8.333	$B_8=$	− 0

s_0	+	−	s_9	+	−
$B_0+B_9=$	10.244		$B_0-B_9=$	10.388	
$B_1+B_8=$		8.629	$-(B_1-B_8)=$	8.037	
$B_2+B_7=$		2.365	$B_2-B_7=$		1.015
$B_3+B_6=$	0.772		$-(B_3-B_6)=$	0.728	
$B_4+B_5=$		0.173	$B_4-B_5=$	0.163	
	11.016	11.167		19.316	1.015
$s_0=$		− 0.151	$s_9=$	18.301	
Actual		− 0.150	*Actual*	18.300	

thing, on the ordinates on which those analyses rest. Their good agreement is therefore to be regarded merely as a check on the two methods and the results of calculation.

EXAMPLE 13. ILLUSTRATING THE RESOLUTION OF A POWER CURVE INTO COMPONENTS

In this example the power curve considered in the preceding example (corresponding to the emf and current curves of Fig. 3) will be resolved into two components. Both systems of resolution, treated on pages 614 and 615, will be employed, (*a*) that in which the emf. is resolved into two components, one in phase with the current, and the other 90° ahead of it, and (*b*) that in which the current is resolved into components, one along the emf vector and the other 90° behind it. The difference in the physical significance of these two methods has been already discussed (pp. 615 to 617).

TABLE 17

Comparison of Equations of Power Curves found by Analysis and by Calculation

	Power curve				Power components							
					ei_1				ei_2			
	Amplitude		Phase ϕ		Amplitude		Phase ϕ		Amplitude		Phase ϕ	
	C	A	C	A	C	A	C	A	C	A	C	A
0	10.314	10.316			11.20	10.878						
2	21.848	21.843	78.8	78.8	(10.142)	10.142	46.6	46.8	(20.185)	20.185	91.4	91.9
4	3.307	3.242	37.1	37.1	1.730	1.524	26.3	26.3	2.448	2.422	43.8	42.4
6	0.962	0.972	0.4	− 0.2	0.715	0.885	51.2	50.1	0.824	0.966	7.6	8.4
8	0.022	0.032	19.4	21.4	0.144	0.103	31.8	30.5	0.145	0.102	10.4	33.6
10	0.353	0.340	15.1	15.0	0.272	0.144	11.5	13.1	0.216	0.218	19.5	20.0
12	0.753	0.750	22.7	22.6	0.583	0.556	26.2	26.5	0.522	0.496	18.9	19.8
14	1.091	1.084	10.1	10.1	1.125	1.058	10.2	10.3	0.065	0.077	9.6	14.9
16	0.960	0.976	1.1	1.1	0.685	0.604	20.5	20.5	0.753	0.839	3.7	3.6
18	0.082		3.7		0.007		2.4		0.075	0.012	3.9	1.6

The methods of calculation, outlined above (pp. 618 and 619), are illustrated in Tables 18 to 23, and should be understood more clearly after an examination of the method of calculation of the power curve, given in the example above.

TABLE 18

Derivation of the Two Components of the Power Curve. Resolution of the Emf Curve and the Current Curve

m Order	$(\delta_m-\theta_m)$	sin $(\delta_m-\theta_m)$	cos $(\delta_m-\theta_m)$	E_m	E'_m	E''_m	I_m	I'_m	I''_m
	°								
1	65.3	0.9085	0.4179	33.217	13.880	30.178	29.627	12.380	−26.916
3	77.2	.9751	.2215	0.970	0.215	0.946	3.866	0.856	− 3.770
5	− 77.8	− .9774	.2113	1.702	.360	−1.663	0.459	.0972	0.448
7	−161.0	− .3256	− .9455	0.218	− .206	− .0710	.211	− .200	.0688
9	84.5	.9954	.0958	0.355	.0360	.353	.155	.0149	− .154
11	− 42.1	− .6704	.7480	0.205	.154	− .137	.163	.121	.109
13	79.8	.9842	.1771	1.251	.221	1.231	.214	.0379	− .210
15	− 6.5	− .1132	.9936	1.528	1.518	− .173	.188	.187	.0212
17	256.9	− .9740	− .2250	0.159	− .0358	− .155	.052	− .0117	.0517

We have first to find the components of the current and emf. just referred to. This is carried out in Table 18. This table contains in the first column the order of the harmonics, in the second the phase differences $(\delta_m-\theta_m)$ between the corresponding harmonics of current and emf (the phase difference is taken positive for a lagging current) and in the third and fourth columns the sines and cosines of these angles. The next columns give the harmonics E_m of the emf wave as found by analysis, and the components E'_m and E''_m, respectively, in phase with the current and 90° ahead of it. Similarly, in column 8 are given the harmonic amplitudes of the current, and in columns 9 and 10 the components I'_m and I''_m, respectively, in phase with the emf. and 90° behind it.

(*a*) **By resolution of the emf curve.**—The components of emf just found are used in Tables 19 and 20 to compute the equations of the power component curves e_1i and e_2i, according to the methods sketched on pages 618 and 619. In the first section of Table 19, which treats of the calculation of the curve e_1i, the products E'_mI_n are shown. Thus, $E'_5I_{13}=0.08$ is found in the column headed by I_{13}, and in the row corresponding to harmonics of order 5.

TABLE 19

Calculation of Equation of Curve of Power Component $e_p i$

(Resolution of Emf Curve)

Order	I_n	E'_m	δ_n	I_1	I_3	I_5	I_7	I_9	I_{11}	I_{13}	I_{15}	I_{17}
1	29.627	13.880	$66^\circ.9$	411.24	53.66	6.38	2.93	2.15	2.26	2.97	2.61	0.72
3	3.866	0.215	83.5	6.37	0.83	0.10	.045	.03	.035	.046	.04	.01
5	0.459	.360	131.0	10.65	1.39	.165	.08	.056	.06	.08	.07	.02
7	.211	−.206	107.1	−6.10	−0.80	−.095	−.04	−.03	−.034	−.04	−.04	−.01
9	.155	.0360	104.6	1.06	0.14	.016	.01	.01	.01	.01	.01	.00
11	.163	.154	169.7	4.57	.595	.07	.03	.02	.025	.03	.03	.01
13	.214	.221	129.1	6.55	.85	.10	.05	.03	.035	.05	.04	.01
15	.188	1.518	229.1	45.03	5.87	.70	.32	.24	.25	.325	.285	.08
17	.052	−.0358	308.0	−1.06	−.14	−.02	−.01	−.01	−.01	−.01	−.01	.00

CALCULATION OF TERM IN 12*pt*

n	m	$E'_m I_n$	$(\delta_n+\delta_m)$	$\pm(\delta_m-\delta_n)$	Amplitudes M	Phase α	$\sin\alpha$	$\cos\alpha$	$M\sin\alpha$	$M\cos\alpha$
1	11	−4.57	$236^\circ.6$		−6.83	236.6	−.8348	−.5505	5.70	3.76
1	13	6.55		62.2	9.52	62.2	.8846	.4664	8.43	4.44
3	9	−0.14	188.1		−0.17	188.1	−.1409	−.9900	0.02	0.17
3	15	5.87		145.6	5.91	145.6	.5650	−.8251	3.34	−4.87
5	7	0.095	238.1		0.015	238.1	−.8490	−.5284	−0.01	−0.01
5	17	−0.02		177.0	0.00	177.0	.0523	−.9985		
7	5	−0.08	238.1							
9	3	−0.03	188.1					Sums=	17.48	3.49
11	1	−2.26	236.6					$N=\sqrt{17.48^2+3.49^2}=17.83$		
13	1	2.97		62.2				$\tan\gamma=\frac{-3.49}{17.48}$		
15	3	0.04		145.6						
17	5	0.02		177.0				$\gamma=348^\circ.7$		

In the second part of the table is shown, in detail, the calculation of the term in 12*pt*. Here those products $E'_m I_n$ enter, for which $(m+n)=12$ (in which case the product is given the negative sign), and those for which $(m-n)=12$, or $(n-m)=12$, the sign being positive in both the latter cases. With regard to the phase, we have as rules, that for $(m+n)=12$ the phase is $(\delta_n+\delta_m)$; for $(m-n)=12$ or $(n-m)=12$, the phase is $\pm(\delta_m-\delta_n)$, the sign being taken positive or negative according as m is greater or less than n. (These rules are exactly the same as in the calculation of the power curve.)

The rest of the calculation is, however, simpler than in the case of the power curve, since here the terms group themselves in pairs, for which the phase difference is the same. The ampli-

TABLE 20

Calculation of the Equation of the Curve of the Wattless Component e_2i of the Power Curve

(Resolution of the Emf Curve)

Order	I_n	E_n'	θ_n	I_1	I_3	I_5	I_7	I_9	I_{11}	I_{13}	I_{15}	I_{17}
1	29.627	30.178	66°9	894.08	116.67	13.85	6.37	4.68	4.925	6.465	5.675	1.57
3	3.866	0.946	83.5	28.08	3.66	0.43	0.20	0.15	0.15	0.20	0.18	0.05
5	0.459	−1.663	131.0	−49.27	−6.425	−0.76	−0.35	−0.26	−0.27	−0.355	−0.31	−0.09
7	0.211	−0.0710	107.1	−2.11	−0.27	−0.03	−0.015	−0.01	−0.01	−0.01	−0.01	−0.00
9	0.155	0.353	104.6	10.46	1.36	0.16	0.07	0.055	0.06	0.075	0.07	0.02
11	0.163	−0.137	169.7	−4.06	−0.53	−0.06	−0.03	−0.02	−0.02	−0.03	−0.03	−0.01
13	0.214	1.231	129.1	36.32	4.76	0.56	0.26	0.19	0.20	0.26	0.23	0.06
15	0.188	−0.173	229.1	−5.155	−0.67	−0.08	−0.035	−0.03	−0.03	−0.04	−0.03	−0.01
17	0.052	0.155	308.0	−4.585	−0.60	−0.07	−0.03	−0.025	−0.025	−0.03	−0.03	−0.01

CALCULATION OF TERM IN 12*pt*

m	n	$E_m'I_n$	$(\theta_m+\theta_n)$	$\pm(\theta_m-\theta_n)$	Amplitudes M	Phases ε	sin ε	cos ε	M sin ε	M cos ε
11	1	− 4.06	236°6		0.865	236.6	−0.8348	−.5505	− 0.72	− 0.48
1	11	4.925	"		−29.855	62.2	.8846	.4664	−26.41	−13.92
13	1	−36.32		62°2	1.51	188.1	− .1409	−.9900	− 0.21	− 1.49
1	13	6.465		"	0.85	145.6	.5650	−.8251	0.48	− 0.70
9	3	1.36	188.1		− 0.38	238.1	− .8490	−.5284	0.32	0.20
3	9	0.15	"		− 0.02	177.0	.0523	.9985		0.02
15	3	0.67		145.6					−26.54	−16.37
3	15	0.18		"						
7	5	− 0.03	238.1							
5	7	− 0.35	"							
17	5	0.07		177.0						
5	17	− 0.09		"						

$$N=\sqrt{\overline{26.54}^2+\overline{16.37}^2}=31.18$$

$$\tan\gamma=\frac{-26.54}{-16.37}$$

$$\gamma=238°4$$

CHECK ON RESOLUTION OF POWER CURVE TERM IN 12*pt*

Component	Amplitudes M	Phases ε	sin ε	cos ε	M sin ε	M cos ε
Power $=e_1i$	17.83	348°7	−0.1959	0.9806	− 3.49	17.48
Wattless $=e_2i$	31.18	238.4	−0.8517	−0.5240	−26.54	−16.37
					−30.03	− 1.11

$$N=\sqrt{\overline{30.03}^2+\overline{1.11}^2}=30.05$$

For power curve
$N=30.12$
$\gamma=271°9$

$$\tan\gamma=\frac{-30.03}{1.11}$$

$$\gamma=272°1$$

tudes M thus grouped, together with their phases α, are given in columns 6 and 7. The sines and cosines of α follow, and the products $M \sin \alpha$ and $M \cos \alpha$. The method of derivation of the amplitude N and the phase γ from these products is evident from the table.

Table 20 treats of the calculation of the equation of the curve of $e_2 i$. The first part of the table shows the calculation of the products $E_m{}''I_n$, the system of arrangement being the same as in the preceding tables. Then follows the detailed calculation of a single term, that in $12pt$. Referring to the equation

$$2 \sin (npt - \delta_n) \cos (mpt - \delta_m) = \sin [(m+n)pt - (\delta_m + \delta_n)] \\ + \sin [(n-m)pt - (\delta_n - \delta_m)]$$

it is evident that those products for which $(m+n) = 12$ enter without change of sign, as well as those for which $(n-m) = 12$, while those for which $(m-n) = 12$ are to be taken with the reversed sign. With regard to the phase, it is $(\delta_m + \delta_n)$ for $(m+n) = 12$, $(\delta_n - \delta_m)$ for $(n-m) = 12$, and $(\delta_m - \delta_n)$ for $(m-n) = 12$.

Here, as in the preceding case, the terms group themselves in pairs which have the same phase. The calculation of the resultant amplitude N and the resultant phase γ is given in detail in the table.

In the last part of Table 20 is given a check on the derivation of the term in $12pt$ for the curves $e_1 i$ and $e_2 i$. The sum of these two terms should equal the term in $12pt$ in the equation of total power (Example 12). This condition is closely realized by the values calculated in Tables 19 and 20, as is here shown, the sum being $30.05 \sin (12pt - 272^\circ.1)$ while the value calculated for the curve of total power in Example 12 is $30.12 \sin (12pt - 271^\circ.9)$. This check is of great value, although, in case it is not realized in any given case, it gives no indication as to which of the curves $e_1 i$ and $e_2 i$ is in error.

(*b*) **By resolution of the Current—Curves ei_1 and ei_2.**—The method of calculation for this case is illustrated in Tables 21 and 22. These tables bear a close resemblance to Tables 19 and 20, respectively, and will be clear from what has been said regarding the arrangement of the latter. Here, as in the preceding case, the calculation has been carried through for the term in

12*pt* and at the end of Table 22 is given a check on the correctness of the terms found in the curves of ei_1 and ei_2.

TABLE 21

Calculation of the Equation of the Curve ei_1. Power Component Resolving the Current

Order	E_m	I_n'	θ_m	E_1	E_3	E_5	E_7	E_9	E_{11}	E_{13}	E_{15}	E_{17}
			°									
1	33.217	12.380	1.6	411.23	12.01	21.07	2.70	4.40	2.54	15.49	18.92	1.97
3	0.970	0.856	6.3	28.43	0.83	1.46	0.19	0.30	0.175	1.07	1.31	0.135
5	1.702	0.0972	208.8	3.23	0.095	0.165	0.02	0.035	0.02	0.12	0.15	0.015
7	0.218	−0.200	268.1	−6.64	−0.195	−0.34	−0.04	−0.07	−0.04	−0.25	−0.31	−0.03
9	0.355	0.0149	20.1	0.50	0.01	0.025	0.00	0.01	0.00	0.02	0.02	0.00
11	0.205	0.121	211.8	4.02	0.12	0.205	0.03	0.04	0.025	0.15	0.185	0.02
13	1.251	0.0379	49.3	1.26	0.04	0.065	0.01	0.01	0.01	0.05	0.06	0.01
15	1.528	0.187	235.6	6.215	0.18	0.32	0.04	0.07	0.04	0.23	0.29	0.03
17	0.159	−0.0117	51.1	−0.39	−0.01	−0.02	−0.00	−0.00	−0.00	−0.015	−0.02	−0.00

CALCULATION OF TERM IN 12*pt*

m	n	E_mI_n'	$(\theta_m+\theta_n)$	$\pm(\theta_m-\theta_n)$	Amplitudes M	Phases α	sin α	cos α	M sin α	M cos α
			°			°				
1	11	− 4.02	213.4		− 6.56	213.4	−.5505	−.8348	3.61	5.47
11	1	− 2.54	"	°	16.75	47.7	.7396	.6730	12.39	11.27
1	13	1.26		47.7	− 0.31	26.4	.4446	.8957	− 0.14	− 0.28
13	1	15.49		"	1.49	229.3	−.7581	−.6521	− 1.13	− 0.97
3	9	− 0.01	26.4		0.32	476.9	.8918	−.4524	0.29	− 0.14
9	3	− 0.30	"		− 0.005	−157.7	−.3795	−.9252		
3	15	0.18		229.3					15.02	15.35
15	3	1.31		"						
5	7	0.34	476.9							
7	5	− 0.02	"							
5	17	− 0.02		−157.7						
17	5	0.015		"						

$$M = \sqrt{\overline{15.02}^2 + \overline{15.35}^2} = 21.48$$

$$\tan \gamma = \frac{-15.35}{15.02}$$

$$\gamma = 314^\circ.3$$

For comparison, the equations of the four curves corresponding to the resolution of the power curve according to these two methods are presented in Table 23.

It will be noticed that the two methods lead to quite different curves. The latter part of the table contains the checks on the curves; that is, it gives an idea of how closely the sums of the two components in each case approaches the value of the power

TABLE 22

Calculation of the Equation of the Curve ei_2. Wattless Component Resolving Current

Order	E_m	I_n''	θ_m	E_1	E_3	E_5	E_7	E_9	E_{11}	E_{13}	E_{15}	E_{17}
1	33.217	−26.916	1.6	−894.08	−26.11	−45.81	−5.87	−9.56	−5.52	−33.68	−41.13	−4.285
3	0.970	− 3.770	6.3	−125.23	− 3.655	− 6.415	−0.82	−1.34	−0.77	− 4.72	− 5.77	−0.60
5	1.702	0.448	208.8	14.82	0.435	0.76	0.10	0.16	0.09	0.56	0.685	0.07
7	0.218	0.0688	268.1	2.28	0.07	0.12	0.015	0.025	0.015	0.085	0.105	0.01
9	0.355	− 0.154	20.1	− 5.12	− 0.15	− 0.26	−0.03	−0.055	−0.03	− 0.19	− 0.235	−0.025
11	0.205	0.109	211.8	3.62	0.105	0.185	0.02	0.04	0.02	0.14	0.17	0.02
13	1.251	− 0.210	49.3	− 6.975	− 0.20	− 0.36	−0.05	−0.075	−0.04	−0.26	− 0.32	−0.03
15	1.528	0.0212	235.6	0.70	0.02	0.04	0.00	0.01	0.00	0.025	0.03	0.00
17	0.159	0.0517	51.1	1.72	0.05	0.09	0.01	0.02	0.01	0.065	0.08	0.01

CALCULATION OF TERM IN 12*pt*

m	n	E_mI_n''	$(\theta_m+\theta_n)$	$\pm(\theta_m-\theta_n)$	Amplitudes M	Phases α	sin α	cos α	M sin α	M cos α
			°			°				
1	11	3.62	213.4		− 1.90	213.4	−0.5505	−0.8348	1.05	1.59
11	1	− 5.52	"	°	−26.705	47.7	.7396	.6730	−19.75	−17.97
1	13	6.975		47.7	− 1.49	26.4	.4446	.8957	− 0.66	− 1.34
13	1	−33.68		"	− 5.79	229.3	− .7581	− .6521	4.39	3.78
3	9	− 0.15	26.4		0.22	476.9	.8918	− .4524	0.20	− 0.10
9	3	− 1.34	"		− 0.02	−157.7	− .3795	− .9252	0.01	0.02
3	15	− 0.02		229.3						
15	3	− 5.77							−14.76	−14.02
5	7	0.12	476.9							
7	5	0.10	"							
5	17	− 0.09		−157.7						
17	5	0.07		"						

$$N=\sqrt{\overline{14.76}^2+\overline{14.02}^2}=20.33$$

$$\tan\gamma=\frac{-14.76}{-14.02}$$

$$\gamma=226^\circ.5$$

CHECK ON RESOLUTION OF POWER CURVE TERM IN 12*pt*

Component	Amplitudes M	Phases α	sin α	cos α	M sin α	M cos α
Power	21.48	314.3	−0.7157	0.6984	−15.35	15.02
Wattless	20.33	226.5	−0.7254	−0.6884	−14.76	−14.02
					−30.11	1.00

From power curve
$N=30.12$
$\gamma=271^\circ.9$

$$N=\sqrt{\overline{30.11}^2+\overline{1.00}^2}=30.12$$

$$\tan\gamma=\frac{-30.11}{1.00}$$

$$\gamma=271^\circ.9$$

curve. The agreement shown in the table is to be regarded as satisfactory, considering the number of significant figures retained in the calculations.

It is of interest to compare these equations with those found by analysis of the curves *C* and *D* of Fig. 3. These were determined experimentally, as described in the introduction, the power attachment of the curve tracer having been set successively to the ordinates of the curves i_1 and i_3 (determined by resolving the analyzed current wave), while the emf of the dynamo was balanced on the curve tracer solenoid. These curves give, therefore, the instantaneous values of ei_1 and ei_3, respectively.

TABLE 23

Comparison of Equations of Components of Power Curve both Resolving the Emf and the Current

Order	e_1i		e_3i		ei_1		ei_3		Checks				Power curve	
									e_1i+e_3i		ei_1+ei_3			
	Amp.	Phase	Amp.	Phase	Amp.	Phase	Amp.	Phase	Amp.	Phase	Amp.	Phase	Amp.	Phase
		°		°		°		°		°		°		°
2	441.7	231.0	858.8	128.1	373.05	93.2	788.23	182.8	873.4	157.6	874.0	157.6	873.9	157.6
4	69.9	256.3	161.9	127.3	63.68	105.1	96.56	175.4	132.4	148.3	132.5	148.4	132.3	148.3
6	15.10	282.8	38.76	25.3	26.32	307.2	32.19	45.4	38.43	2.8	38.52	2.9	38.46	2.6
8	4.07	350.1	4.79	167.8	5.30	254.8	5.64	83.1	0.75	155.4	0.82	157.8	0.88	155.2
10	7.76	349.0	21.61	157.5	10.03	115.4	8.42	195.4	14.08	151.6	14.17	151.2	14.13	151.4
12	17.83	348.7	31.18	298.4	21.48	314.3	20.33	226°5	30.05	272.1	30.12	271.9	30.12	271.9
14	40.10	63.5	52.47	189.3	41.47	143.2	2.54	113.4	43.57	141.0	43.70	141.5	43.66	141.2
16	48.06	24.6	10.91	229.2	25.22	328.5	20.41	59.2	38.45	17.8	38.49	18.3	38.38	18.2
18	5.68	88.4	3.39	191.6	0.36	43.5	2.93	69.4	3.24	66.7	3.16	67.3	3.26	67.1

The experimental curves were analyzed by Schedule 3, Appendix B, and the results obtained will be found in Table 17 along with the calculated values given in Table 23, the amplitudes of the latter having been reduced by a factor so as to agree with the scale of the curves. The calculated values are indicated by the letter *C*, those found by analysis by the letter *A*. The phases are all reduced to the scale of the fundamental of the emf. and current waves. The agreement of the curves found by the two methods is probably as good as could be expected.

No claim is made to anything approaching completeness in the list of applications here considered. Others will, no doubt, occur to readers engaged in this kind of work, and modifications of the procedure may have to be made to fit special cases. However, the author hopes that the treatment here given will not only be of material service in lightening the labor of ordinary routine calculations, but may be broad enough to cover the general methods which must be followed in attacking special problems.

VII. SUMMARY

1. The equations of Fourier for the resolution of a periodic curve into a series of component sine curves, although furnishing a complete solution of the problem, suffer under the disadvantage that, in making numerical calculations, a large number of products have to be formed. Consequently, other less satisfactory methods have been employed to shorten the calculation. By grouping similar terms, Runge has so simplified the use of the Fourier equations as to greatly reduce the labor of calculation. The object of this paper is to stimulate a more general employment of Runge's method by the systematic arrangement of the calculations and the use of multiplication tables such as to render inconsiderable the time and labor necessary for the precise analysis of alternating current curves.

2. The derivation of Fourier's equations for the case of a finite number of odd harmonics is sketched briefly, using the treatment in Byerly's "Fourier's Series and Spherical Harmonics," and this is followed by a development of the simplifications introduced by Runge.

3. The arrangement of the calculation is given in detail for three special cases, namely, for 6, 12, and 18 measured ordinates per half cycle, together with check equations which facilitate the location of numerical errors. The considerations which determine the choice of the proper schedule of analysis in any given case are treated at some length.

4. The complete calculation of the amplitude and phases of the component waves of experimentally determined alternating current curves is carried through, using each of the three schemes of analysis. Further examples are given in connection with what has been previously enunciated with respect to the choice of schedule and to illustrate the accuracy of the results.

5. The latter part of the paper is devoted to the consideration of a few practical applications, such as the calculation of average and effective values, average power, and equations of power curves, together with a full illustration of the principles involved in numerical examples.

6. In an appendix are given multiplication tables, from which may be taken the products which have to be formed in the use of the three analysis schedules. Further analysis schedules are added for curves in which even harmonics are present, which schedules may therefore be used for the analysis of power curves.

WASHINGTON, May 15, 1913.

APPENDIXES

APPENDIX A

TABLE 1

Multiplication Table for Use with the Six-Point and Eighteen-Point Analysis Schedules

	sin 10°	sin 20°	sin 30°	sin 40°	sin 50°	sin 60°	sin 70°	sin 80°
1	0.1736	0.3420	0.5000	0.6428	0.7660	0.8660	0.9397	0.9848
2	0.3473	0.6840	1.000	1.2855	1.532	1.732	1.879	1.970
3	0.5209	1.026	1.500	1.928	2.298	2.598	2.819	2.954
4	0.6946	1.368	2.000	2.571	3.064	3.464	3.759	3.939
5	0.8682	1.710	2.500	3.214	3.830	4.330	4.6985	4.924
6	1.042	2.052	3.000	3.857	4.596	5.196	5.638	5.909
7	1.2155	2.394	3.500	4.4995	5.362	6.062	6.578	6.894
8	1.389	2.736	4.000	5.142	6.128	6.928	7.518	7.878
9	1.563	3.078	4.500	5.785	6.894	7.794	8.457	8.863
10	1.7365	3.420	5.000	6.428	7.660	8.660	9.397	9.848
11	1.910	3.762	5.500	7.0705	8.4265	9.526	10.337	10.833
12	2.084	4.104	6.000	7.713	9.1925	10.392	11.276	11.818
13	2.2575	4.446	6.500	8.356	9.9585	11.258	12.216	12.802
14	2.431	4.788	7.000	8.999	10.7245	12.124	13.156	13.787
15	2.605	5.130	7.500	9.642	11.491	12.990	14.0955	14.772
16	2.778	5.472	8.000	10.2845	12.257	13.856	15.035	15.757
17	2.952	5.814	8.500	10.927	13.023	14.722	15.975	16.742
18	3.126	6.156	9.000	11.570	13.789	15.588	16.915	17.726
19	3.299	6.498	9.500	12.213	14.555	16.454	17.854	18.711
20	3.473	6.8405	10.000	12.856	15.321	17.320	18.794	19.696
21	3.647	7.1825	10.500	13.498	16.087	18.1865	19.734	20.681
22	3.820	7.5245	11.000	14.141	16.853	19.0525	20.673	21.666
23	3.994	7.8665	11.500	14.784	17.619	19.9185	21.613	22.650
24	4.168	8.2085	12.000	15.427	18.385	20.7845	22.553	23.635
25	4.341	8.5505	12.500	16.0695	19.151	21.6505	23.4925	24.620
26	4.515	8.8925	13.000	16.712	19.917	22.5165	24.432	25.605
27	4.6885	9.2345	13.500	17.355	20.683	23.3825	25.372	26.590
28	4.862	9.5765	14.000	17.998	21.449	24.2485	26.312	27.574
29	5.036	9.9185	14.500	18.641	22.215	25.1145	27.251	28.559
30	5.2095	10.027	15.000	19.283	22.981	25.981	28.191	29.544
31	5.383	10.608	15.500	19.926	23.757	26.847	29.131	30.529
32	5.557	10.945	16.000	20.569	24.513	27.713	30.070	31.514
33	5.7305	11.287	16.500	21.212	25.279	28.579	31.010	32.498
34	5.904	11.629	17.000	21.8545	26.045	29.445	31.950	33.483
35	6.078	11.971	17.500	22.497	26.811	30.311	32.8895	34.468
36	6.251	12.313	18.000	23.140	27.577	31.177	33.829	35.453
37	6.425	12.655	18.500	23.783	28.3435	32.043	34.769	36.438
38	6.599	12.997	19.000	24.426	29.1095	32.909	35.709	37.422
39	6.772	13.339	19.500	25.068	29.8755	33.775	36.648	38.407
40	6.946	13.681	20.000	25.711	30.642	34.641	37.588	39.392
41	7.120	14.023	20.500	26.354	31.408	35.507	38.528	40.377
42	7.293	14.365	21.000	26.997	32.174	36.373	39.467	41.362
43	7.467	14.707	21.500	27.6395	32.940	37.239	40.407	42.346
44	7.641	15.049	22.000	28.282	33.706	38.105	41.347	43.331
45	7.814	15.391	22.500	28.925	34.472	38.971	42.2865	44.316
46	7.988	15.733	23.000	29.568	35.238	39.837	43.226	45.301
47	8.1615	16.075	23.500	30.211	36.004	40.703	44.166	46.286
48	8.335	16.417	24.000	30.8535	36.770	41.569	45.106	47.270
49	8.509	16.759	24.500	31.496	37.536	42.435	46.045	48.255
50	8.6825	17.101	25.000	32.139	38.302	43.301	46.985	49.240

TABLE 1—Continued

	sin 10°	sin 20°	sin 30°	sin 40°	sin 50°	sin 60°	sin 70°	sin 80°
51	8.856	17.443	25.500	32.782	39.068	44.167	47.925	50.225
52	9.030	17.785	26.000	33.4245	39.834	45.033	48.864	51.210
53	9.2035	18.127	26.500	34.067	40.600	45.899	49.864	52.194
54	9.377	18.469	27.000	34.710	41.366	46.765	50.744	53.179
55	9.551	18.811	27.500	35.353	42.132	47.631	51.6835	54.164
56	9.724	19.153	38.068	35.996	42.898	48.497	52.623	55.149
57	9.898	19.495	28.500	36.6385	43.664	49.363	53.563	56.134
58	10.072	19.837	29.000	37.281	44.430	50.229	54.563	57.118
59	10.245	20.180	29.500	37.924	45.196	51.095	55.442	58.103
60	10.419	20.521	30.000	38.567	45.962	51.961	56.382	59.088
61	10.593	20.863	30.500	39.210	46.7285	52.827	57.322	60.073
62	10.766	21.205	31.000	39.852	47.4945	53.693	58.261	61.058
63	10.940	21.547	31.500	40.495	48.2605	54.559	59.201	62.042
64	11.114	21.889	32.000	41.138	49.0265	55.425	60.141	63.027
65	11.287	22.231	32.500	41.781	49.793	56.291	61.0805	64.012
66	11.461	22.573	33.000	42.4235	50.559	57.157	62.020	64.997
67	11.6345	22.915	33.500	43.066	51.325	58.023	62.960	65.982
68	11.808	23.257	34.000	43.709	52.091	58.889	63.960	66.966
69	11.982	23.599	34.500	44.352	52.857	59.755	64.839	67.951
70	12.1555	23.9415	35.000	44.995	53.623	60.621	65.779	68.936
71	12.329	24.2835	35.500	45.637	54.389	61.487	66.719	69.921
72	12.503	24.6255	36.000	46.280	55.155	62.353	67.658	70.906
73	12.676	24.9675	36.500	46.923	55.921	63.2195	68.598	71.890
74	12.850	25.3095	37.000	47.566	56.687	64.0855	69.538	72.875
75	13.024	25.6515	37.500	48.2085	57.453	64.9515	70.4775	73.860
76	13.197	25.9935	38.000	48.851	58.219	65.8175	71.417	74.845
77	13.371	26.3355	38.500	49.494	58.984	66.6835	72.357	75.830
78	13.545	26.6775	39.000	50.137	59.751	67.5495	73.297	76.814
79	13.718	27.0195	39.500	50.780	60.517	68.420	74.236	77.799
80	13.892	27.362	40.000	51.422	61.283	69.382	75.176	78.784
81	14.066	27.704	40.500	52.065	62.049	70.148	76.116	79.769
82	14.239	28.046	41.000	52.708	62.815	71.014	77.055	80.754
83	14.413	28.388	41.500	53.351	63.581	71.000	77.995	81.738
84	14.587	28.730	42.000	53.9935	64.347	72.746	78.935	82.723
85	14.760	29.072	42.500	54.636	65.113	73.612	79.8745	83.708
86	14.934	29.414	43.000	55.279	65.879	74.478	80.814	84.693
87	15.1075	29.756	43.500	55.922	66.6455	75.344	81.754	85.678
88	15.281	30.098	44.000	56.565	67.4115	76.210	82.694	86.662
89	15.455	30.440	44.500	57.207	68.1775	77.076	83.633	87.647
90	15.6285	30.782	45.000	57.850	68.944	77.942	84.573	88.632
91	15.802	31.124	45.500	58.493	69.710	78.808	85.513	89.617
92	15.976	31.466	46.000	59.136	70.476	79.674	86.452	90.602
93	16.1495	31.808	46.500	59.7785	71.242	80.540	87.392	91.586
94	16.323	32.150	47.000	60.421	72.008	81.406	88.332	92.571
95	16.497	32.492	47.500	61.064	72.774	82.272	89.2715	93.556
96	16.670	32.834	48.000	61.707	73.540	83.138	90.211	94.541
97	16.844	33.176	48.500	62.350	74.306	84.004	91.151	95.526
98	17.018	33.518	49.000	62.992	75.072	84.870	92.091	96.510
99	17.191	33.860	49.500	63.635	75.838	85.736	93.030	97.495
100	17.365	34.202	50.000	64.278	76.604	86.602	93.970	98.480

TABLE 2

Multiplication Table for Use with the 12-Point Analysis Schedule

	sin 15°	sin 45°	sin 75°		sin 15°	sin 45°	sin 75°
1	0. 2588	0. 7071	0. 9659	51	13. 200	36. 068	49. 262
2	0. 5176	1. 414	1. 932	52	13. 459	36. 770	50. 228
3	0. 7765	2. 121	2. 898	53	13. 7175	37. 477	51. 194
4	1. 035	2. 828	3. 864	54	13. 976	38. 184	52. 160
5	1. 294	3. 5355	4. 830	55	14. 235	38. 891	53. 126
6	1. 553	4. 243	5. 796	56	14. 494	39. 598	54. 092
7	1. 812	4. 950	6. 7615	57	14. 753	40. 305	55. 058
8	2. 071	5. 657	7. 727	58	15. 012	41. 012	56. 024
9	2. 329	6. 364	8. 693	59	15. 270	41. 7195	56. 990
10	2. 588	7. 071	9. 659	60	15. 529	42. 427	57. 956
11	2. 847	7. 778	10. 625	61	15. 788	43. 134	58. 922
12	3. 106	8. 485	11. 591	62	16. 047	43. 841	59. 888
13	3. 365	9. 192	12. 557	63	16. 306	44. 548	60. 854
14	3. 6235	9. 8995	13. 523	64	16. 5645	45. 255	61. 8195
15	3. 882	10. 607	14. 489	65	16. 823	45. 962	62. 785
16	4. 141	11. 314	15. 455	66	17. 082	46. 669	63. 751
17	4. 400	12. 021	16. 421	67	17. 341	47. 336	64. 717
18	4. 659	12. 728	17. 387	68	17. 600	48. 0835	65. 683
19	4. 918	13. 435	18. 353	69	17. 859	48. 791	66. 649
20	5. 176	14. 142	19. 319	70	18. 117	49. 498	67. 615
21	5. 435	14. 849	20. 2845	71	18. 376	50. 205	68. 581
22	5. 694	15. 556	21. 2505	72	18. 635	50. 912	69. 547
23	5. 953	16. 2635	22. 216	73	18. 894	51. 619	70. 513
24	6. 212	16. 971	23. 182	74	19. 153	52. 326	71. 479
25	6. 4705	17. 678	24. 148	75	19. 4115	53. 033	72. 445
26	6. 729	18. 385	25. 114	76	19. 670	53. 740	73. 411
27	6. 988	19. 092	26. 080	77	19. 929	54. 4475	74. 377
28	7. 247	19. 799	27. 046	78	20. 188	55. 155	75. 3425
29	7. 506	20. 506	28. 012	79	20. 447	55. 862	76. 3085
30	7. 765	21. 213	28. 978	80	20. 706	56. 569	77. 274
31	8. 023	21. 920	29. 944	81	20. 964	57. 276	78. 240
32	8. 282	22. 6275	30. 910	82	21. 223	57. 983	79. 206
33	8. 541	23. 335	31. 876	83	21. 482	58. 690	80. 172
34	8. 800	24. 042	32. 842	84	21. 741	59. 397	81. 138
35	9. 059	24. 749	33. 8075	85	22. 000	60. 104	82. 104
36	9. 3175	25. 456	34. 7735	86	22. 2585	60. 8115	83. 070
37	9. 576	26. 163	35. 739	87	22. 517	61. 519	84. 036
38	9. 835	26. 870	36. 705	88	22. 776	62. 226	85. 002
39	10. 094	27. 577	37. 671	89	23. 035	62. 933	85. 968
40	10. 353	28. 284	38. 637	90	23. 294	63. 640	86. 934
41	10. 612	28. 9915	39. 603	91	23. 553	64. 347	87. 900
42	10. 870	29. 699	40. 569	92	23. 811	65. 054	88. 866
43	11. 129	30. 406	41. 535	93	24. 070	65. 761	89. 8315
44	11. 388	31. 113	42. 501	94	24. 329	66. 468	90. 797
45	11. 647	31. 820	43. 467	95	24. 588	67. 175	91. 763
46	11. 906	32. 527	44. 433	96	24. 847	67. 883	92. 729
47	12. 1645	33. 234	45. 399	97	25. 1055	68. 590	93. 695
48	12. 423	33. 941	46. 365	98	25. 364	69. 297	94. 661
49	12. 682	34. 648	47. 331	99	25. 623	70. 004	95. 627
50	12. 941	35. 3555	48. 2965	100	25. 882	70. 711	96. 593

APPENDIX B

ANALYSIS OF CURVES CONTAINING EVEN HARMONICS AND A CONSTANT TERM. (POWER CURVES)

In this section is considered the analysis of curves which are capable of being represented by an equation of the form

$$\begin{aligned}y = B_0 + B_1 \cos pt + B_2 \cos 2pt + B_3 \cos 3pt + \ . \ . \ . \ + B_n \cos npt \\ + A_1 \sin pt + A_2 \sin 2pt + A_3 \sin 3pt + \ . \ . \ . \ + A_n \sin npt.\end{aligned}$$

The fundamental ordinates are supposed to be $2n$ in number, equally spaced over the whole cycle. (In the analysis of current and electromotive force curves, we have constantly used fundamental ordinates equally spaced over the *half* cycle.)

What follows has been arranged with special reference to the analysis of power curves. These are represented by equations like that above, the frequency of the fundamental of the power curve being twice that of the fundamental of the emf. or current, and one complete cycle corresponds to a half cycle of the emf. or current. If, therefore, the analysis is being made of the emf. and current, it is only necessary for obtaining the equation of the power curve also, to take the products of the corresponding fundamental ordinates used for the analysis of the current and emf. and perform on these the operations indicated in the analysis schedules below. This does not require that the power curve shall have been drawn.

The schemes of analysis for power curves here given have been selected to correspond with those already given for current and emf. curves. Thus, if these have been analyzed by means of the 12-point schedule, Table 2, then the power curve will be obtained using the 12-point schedule in Table 2 below, etc. Such an analysis does not give as complete an equation for the power as may be obtained by taking the product of the equations of emf. and current (p. 612). For example, the product of the equations of emf. and current, obtained by the use of the 18-point schedule will contain harmonics of 34 times the frequency of the fundamental, while the term of highest order given by the analysis of the power curve, Table 3 below, has a frequency only 18 times that of the fundamental. In all cases, however, except those where the higher harmonics in the current and emf. waves are abnormally prominent, all terms beyond those included in the analysis will be negligible.

It may be shown as was done for equation (2) that the coefficients in the above equation are given by the following equations

$$A_k = \frac{1}{n}\sum_{0}^{2n-1} y_m \sin km\frac{\pi}{n}$$

$$B_k = \frac{1}{n}\sum_{0}^{2n-1} y_m \cos km\frac{\pi}{n} \qquad k = 1, 2, \ldots (n-1)$$

$$B_0 = \frac{1}{2n}\sum_{0}^{2n-1} y_m \qquad B_n = \frac{1}{2n}\sum_{0}^{2n-1} (-1)^m y_m$$

The analysis from the $2n$ fundamental ordinates does not allow of the determination of A_n. This can, however, be easily found by measuring another set of ordinates z_m, situated half way between those which are used in the analysis, and substituting them in the equation

$$A_n = \frac{1}{2n}\sum_{0}^{2n-1} (-1)^m z_m$$

The following schedules for facilitating calculations with these equations, for the cases of 6, 12, and 18 measured ordinates, respectively, follow the method of Runge, as in the preceding analysis schedules in Tables 1, 2, and 3, The same multiplication table (Appendix A) may be used as in those cases. For an example of a numerical calculation, see example 12*b*.

SCHEDULE 1

Analysis of a Curve, Involving Even Harmonics and a Constant Term, from Six Ordinates

Arrange the measured ordinates according to the following scheme and take the sums and differences indicated:

	y_0	y_1	y_2	y_3	
		y_5	y_4		
Sums	s_0	s_1	s_2	s_3	$s_0+s_2=\Sigma_0$
Diffs	d_0	d_1	d_2	d_3	$s_1+s_3=\Sigma_1$

(the sum $s_0=d_0=y_0$, but this nomenclature is adhered to for uniformity.)

The coefficients are those given in the schedule below, the arrangement being the same as in the previous schedules—Table 1, 2, and 3:

	sine terms		cosine terms			
	A_1 and A_2		B_1 and B_2		B_0 and B_3	
sin 30°			$-s_2$	s_1		
sin 60°	s_1	s_2				
sin 90°			s_0	$-s_3$	Σ_0	Σ_1
Sums	S_0'	S_e'	S_0''	S_e''	S_0'''	S_e'''
		$A_1=\frac{S_0'+S_e'}{3}$		$B_1=\frac{S_0''+S_e''}{3}$		$B_0=\frac{S_0'''+S_e'''}{6}$
		$A_2=\frac{S_0'-S_e'}{3}$		$B_2=\frac{S_0''-S_e''}{3}$		$B_3=\frac{S_0'''-S_e'''}{6}$

CHECKS

$s_0=(B_0+B_3)+(B_1+B_2)$

$s_2=2(B_0+B_3)-(B_1+B_2)$

$s_0+s_2=3(B_0+B_3)$ $2s_0-s_2=3(B_1+B_2)$

$s_1=2(B_0-B_3)+(B_1-B_2)$

$s_3=(B_0-B_3)-(B_1-B_2)$

$s_1+s_3=3(B_0+B_3)$ $s_1-2s_3=3(B_1-B_2)$

$d_1=2(A_1+A_2)$ sin 60°

$d_2=2(A_1-A_2)$ sin 60°

The first equation checks the sums of the *B's*. If it is not fulfilled, equations may be used in which these sums appear singly. The same procedure is to be adopted with the differences of the *B's*. The sum and difference of the *A's* occur singly. These checks serve as a control on the values of S_0 and S_e.

SCHEDULE 2

Analysis of a Curve, Involving Even Harmonics and a Constant Term, from Twelve Ordinates

MEASURED ORDINATES

	y_0 y_1 y_2 y_3 y_4 y_5 y_6	s_0 s_1 s_2 s_3	d_0 d_1 d_2 d_3
	y_{11} y_{10} y_9 y_8 y_7	s_6 s_5 s_4	d_6 d_5 d_4
Sums	s_0 s_1 s_2 s_3 s_4 s_5 s_6	Sums Σ_0 Σ_1 Σ_2 Σ_3	σ_0 σ_1 σ_2 σ_3 Sums
Diffs.	d_0 d_1 d_2 d_3 d_4 d_5 d_6	Diffs. Δ_0 Δ_1 Δ_2 Δ_3	δ_0 δ_1 δ_2 δ_3 Diffs.

	sine terms				
	A₁ and A₅		A₂ and A₄		A₃
sin 30°	σ_1				
sin 60°		σ_2	δ_1	δ_2	
sin 90°	σ_3				$(\sigma_1-\sigma_3)$
Sums	S_o'	S_e'	S_o''	S_e''	S_o'''
	$A_1=\frac{S_o'+S_e'}{6}$		$A_2=\frac{S_o''+S_o''}{6}$		$A_3=\frac{S_o'''}{6}$
	$A_5=\frac{S_o'-S_e'}{6}$		$A_4=\frac{S_o''-S_e''}{6}$		

	cosine terms						
	B₁ and B₅		B₂ and B₄		B₃	B₀ and B₆	
sin 30°	Δ_2		$-\Sigma_2$	Σ_1			
sin 60°		Δ_1					
sin 90°	Δ_0		Σ_0	$-\Sigma_3$	$(\Delta_0-\Delta_2)$	$(\Sigma_0+\Sigma_2)$	$(\Sigma_1+\Sigma_3)$
Sums	D_o'	D_e'	D_o''	D_e''	D_o'''	D_o''''	D_e''''
	$B_1=\frac{D_o'+D_e'}{6}$		$B_2=\frac{D_o''+D_e''}{6}$		$B_3=\frac{D_o'''}{6}$	$B_0=\frac{D_o''''+D_e''''}{12}$	
	$B_5=\frac{D_o'-D_e'}{6}$		$B_4=\frac{D_o''-D_e''}{6}$			$B_6=\frac{D_o''''-D_e''''}{12}$	

CHECKS

$\Sigma_0 = \quad (B_0+B_6)+(B_1+B_5)+(B_2+B_4)+B_3$

$\Sigma_0 = 2[(B_0+B_6)+(B_2+B_4)]$

$\Delta_0 = 2[(B_1+B_5)+B_3]$

$\Sigma_1 = 4\ (B_0-B_6)+2(B_2-B_4)$

$\Delta_1 = 4\ (B_1-B_5)\ \sin 60°$

$\sigma_1 = 2\ (A_1+A_5)+4A_3$

$\delta_1 = 4\ (A_2+A_4)\ \sin 60°$

$\sigma_2 = 4\ (A_1-A_5)\ \sin 60°$

$\delta_2 = 4\ (A_2-A_4)\ \sin 60°$

SCHEDULE 3

Analysis of a Curve Involving Even Harmonics and a Constant Term from Eighteen Ordinates

MEASURED ORDINATES

	y_0	y_1	y_2	y_3	y_4	y_5	y_6	y_7	y_8	y_9
		y_{17}	y_{16}	y_{15}	y_{14}	y_{13}	y_{12}	y_{11}	y_{10}	
Sums	s_0	s_1	s_2	s_3	s_4	s_5	s_6	s_7	s_8	s_9
Diffs	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9

$d_1-d_5+d_7=\triangle_1$ · $\Sigma_0+\Sigma_2=\partial_0$

$d_2-d_4+d_8=\triangle_2$ $\Sigma_1+\Sigma_3=\partial_1$

$s_0+s_6=\Sigma_0$

$s_3+s_9=\Sigma_3$

$s_1+s_5+s_7=\Sigma_1$

$s_2+s_4+s_8=\Sigma_2$

	Sine terms			
	A_1 and A_8	A_2 and A_7	A_3 and A_6	A_4 and A_5
sin 20°	d_1 d_8	$-d_5$ d_4		$-d_7$ d_2
sin 40°	d_7 d_2	d_1 $-d_8$		d_5 $-d_4$
sin 60°	d_3 d_6	d_3 $-d_6$	$\triangle_1$ $\triangle_2$	$-d_3$ d_6
sin 80°	d_5 d_4	$-d_7$ d_2		d_1 $-d_8$
Sums	D_o D_e $A_1=\frac{D_o+D_e}{9}$ $A_8=\frac{D_o-D_e}{9}$	D_o' D_e' $A_2=\frac{D_o'+D_e'}{9}$ $A_7=\frac{D_o'-D_e'}{9}$	D_o'' D_e'' $A_3=\frac{D_o''+D_e''}{9}$ $A_6=\frac{D_o''-D_e''}{9}$	D_o''' D_e''' $A_4=\frac{D_o'''+D_e'''}{9}$ $A_5=\frac{D_o'''-D_e'''}{9}$

	Cosine terms				
	B_1 and B_8	B_2 and B_7	B_3 and B_6	B_4 and B_5	B_0 and B_9
sin 10°	s_4 $-s_5$	s_2 s_7		s_8 s_1	
sin 30°	$-s_6$ s_3	$-s_6$ $-s_3$	$-\Sigma_2$ Σ_1	$-s_6$ $-s_3$	
sin 50°	s_2 $-s_7$	s_8 s_1		s_4 s_5	
sin 70°	$-s_8$ s_1	$-s_4$ $-s_5$		$-s_2$ $-s_7$	
sin 90°	s_0 $-s_9$	s_0 s_9	Σ_0 $-\Sigma_3$	s_0 s_9	∂_0 ∂_1
Sums	S_o S_e $B_1=\frac{S_o+S_e}{9}$ $B_8=\frac{S_o-S_e}{9}$	S_o' S_e' $B_2=\frac{S_o'+S_e'}{9}$ $B_7=\frac{S_o'-S_e'}{9}$	S_o'' S_e'' $B_3=\frac{S_o''+S_e''}{9}$ $B_6=\frac{S_o''-S_e''}{9}$	S_o''' S_e''' $B_4=\frac{S_o'''+S_e'''}{9}$ $B_5=\frac{S_o'''-S_e'''}{9}$	S_o'''' S_e'''' $B_0=\frac{S_o''''+S_e''''}{18}$ $B_9=\frac{S_o''''-S_e''''}{18}$

CHECKS

$s_0=(B_0+B_9)+(B_1+B_8)+(B_2+B_7)+(B_3+B_6)+(B_4+B_5)$

$s_9=(B_0-B_9)-(B_1-B_8)+(B_2-B_7)-(B_3-B_6)+(B_4-B_5)$

$d_3=2[(A_1+A_8)+(A_2+A_7)-(A_4+A_5)]\sin 60°$

$d_6=2[(A_1-A_8)-(A_2-A_7)+(A_4-A_5)]\sin 60°$

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